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The Infrared Absorption Spectrum of the Deuterium Sulfides

ALVIN H. NIELSEN
University of Tennessee, Knoxville, Tennessee
AND
HARALD H. NIELSEN
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

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The spectra of HDS and D_2S have been investigated under high dispersion using a grating spectrometer. An absorption band at 9.0μ in HDS has been identified as ν_2 and has an average spacing of the rotation lines of about 6.85 cm^{-1}. In D_2S bands were located at 3.75μ, 5.0μ and 10.7μ which have line spacings of 4.8 cm^{-1}, 5.0 cm^{-1}, 5.0 cm^{-1} and may be identified as $\nu_1+\nu_2$, ν_3 corresponding to a similar identification in H_2S. As in H_2S, ν_2 appears to have a Q branch while ν_3 does not. If this is actually so, ν_2 must arise from a vibration of the electric moment parallel with the axis of least moment of inertia and ν_3 from a vibration along the middle axis. Since ν_2 is a vibration parallel with the symmetry axis of the triangle then this axis must be identified with the axis of least moment of inertia. This argument supports the acute angled model suggested by Sprague and Nielsen, and the evidence is interpreted to favor a vertex angle of 85° instead of the 110° angle of Bailey, Thompson and Hale.

I. INTRODUCTION

THE spectrum of the water molecule has perhaps been more completely studied in the infrared than any other triatomic molecule. Due to its intense absorption of radiation a host[1] of bands have been accurately located throughout the spectrum from the photographic region to beyond 6.5μ, all of which have been investigated under high dispersion. This wealth of data supplemented by similar, though less extensive measurements on the HDO and D_2O[2] molecules has made it possible to adopt a quite convincing model for the water vapor molecule.

It would be desirable to pursue a similar course with the hydrogen sulfide molecule, but unfortunately this gas absorbs very unwillingly and its spectrum is only imperfectly known. Two bands at 2.7μ and 3.8μ have been mapped by Nielsen and Barker[3] and a third near 8.0μ was located by Rollefson.[4] Recently the 3.8μ region and the 8.0μ region have been carefully remeasured by Sprague and Nielsen[5] and while nothing new was found at 3.8μ the band of 8.0μ presented an entirely different appearance, although in general verifying the line positions given by Rollefson. Two other bands have been observed by Cross[6] in the photographic infrared at 9911 cm^{-1} and 10,100 cm^{-1}. These he has subjected to a rotational analysis, thereby determining values for the moments of inertia.

[1] W. W. Sleator, Astrophys J. **48**, 125 (1918); Sleator and Phelps, Astrophys J. **62**, 28 (1926); E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931); R. Mecke, Zeits. f. physik. Chemie, Abt. **B16**, 6, 409 and 17.1, 1 (1932); R. Mecke and W. Baumann, Physik. Zeits. **33**, 833 (1932).

[2] E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).

[3] H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931).

[4] A. H. Rollefson, Phys. Rev. **34**, 604 (1929).

[5] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937).

[6] P. C. Cross, Phys. Rev. **47**, 7 (1935).

Very recently one of these regions has been rephotographed by Carvin[7] who finds several of Cross' strong lines to be missing from the spectrum. This, of course, casts some doubt upon the validity of Cross' work and his values for the moments of inertia. In addition to this data a Raman line has been reported by Bhagavantam[8] at 2615 cm^{-1}.

These bands do not, without further assumptions, suffice to fix the shape of the molecule. Neither does a knowledge of the actual values of the moments of inertia alone serve uniquely to determine the shape of the molecule since there will always be two isoceles triangular models, an acute and an obtuse, which will satisfy any set of moments of inertia. If, however, the values of these are known and in addition the rotational character of at least one fundamental band, correctly identified, can be decided upon (i.e., whether, for example, it contains P, Q and R branches or not) then the shape may be uniquely fixed. This may be seen in the following manner. In the XY_2 type molecule three modes of oscillation are possible, two of which ν_1 and ν_2 are parallel to the axis of symmetry of the molecule and the third ν_3, which is normal to it. Since in general ν_1 and ν_3 take values relatively high to ν_2, the latter fundamental may usually be identified without difficulty. If now its rotational characteristics can be decided upon then it is at once determined how the axes of inertia of the molecule will lie. For example, if ν_2 has P, Q and R branches, it must be an oscillation along the axis of the smallest moment of inertia. Since it is also an oscillation along the axis of symmetry, the axis of smallest moment of inertia and the axis of symmetry must be the same. If on the other hand the band does not contain P, Q and R branches it must be an oscillation along the axis of the intermediate moment of inertia and consequently the axis of symmetry must in this case be the axis of the intermediate moment of inertia. It is with the object in view of obtaining further information regarding the shape of the hydrogen sulfide molecule from the rotational character of the absorption bands that we have undertaken this study of the HDS and D_2S spectrum.

[7] F. D. Carvin, J. Chem. Phys. **5**, 159 (1937).
[8] Bhagavantam, Nature **126**, 502 (1930).

II. Apparatus

A prism grating spectrometer having a collimating mirror of two-meter focal length was available for the investigation. The recording apparatus of the spectrometer consisted of a highly sensitive vacuum thermocouple, constructed by Mr. Paul Weyrich of the University of Michigan technical staff, used in conjunction with a Moll thermal relay and a Leeds and Northrup high sensitivity galvanometer. Two echelette gratings ruled by Professor R. W. Wood at Johns Hopkins University were used in analyzing the spectra. The bands at 3.75μ were measured in first order of a 3600-lines-per-inch grating while the bands at 9.0μ and 10.7μ were measured in first order of a grating having 800 lines per inch. The latter grating was used in second order for the 5.0μ region.

The D_2S was made in a vacuum system by dropping 99.2 percent heavy water on the purest obtainable aluminum sulfide and trapping out any heavy water vapor by means of a liquid-air bath. The HDS was made in the same way but 55 percent heavy water was substituted for the 99.2 percent variety. The ensuing gas was therefore a mixture composed of about 25 percent H_2S, 25 percent D_2S and 50 percent HDS. It is believed that some aluminum carbide occurred in the aluminum sulfide as an impurity because of two peaks found in the spectrum of D_2S which correspond to the Q branches of CD_4.[9]

The absorption cells were of glass tubing 30 cm long and 5 cm in diameter and have a stopcock sealed in for evacuating and admitting the gas. The ends were closed with windows of polished rocksalt coated thinly with gum damar to protect them against clouding in the humid weather prevailing while most of these measurements were made.

III. Experimental Results

HDS

In our preliminary paper[10] we reported bands in the spectrum of HDS at 2.1μ, 3.1μ, 4.1μ and 9.0μ. The band at 2.1μ is quite weak and has not been investigated under high dispersion.

[9] H. H. Nielsen and A. H. Nielsen, Abstract No. 29, Chicago meeting of the Am. Phys. Soc. Nov. 27, 1936.
[10] A. H. Nielsen and H. H. Nielsen, J. Chem. Phys. **4**, 229 (1936).

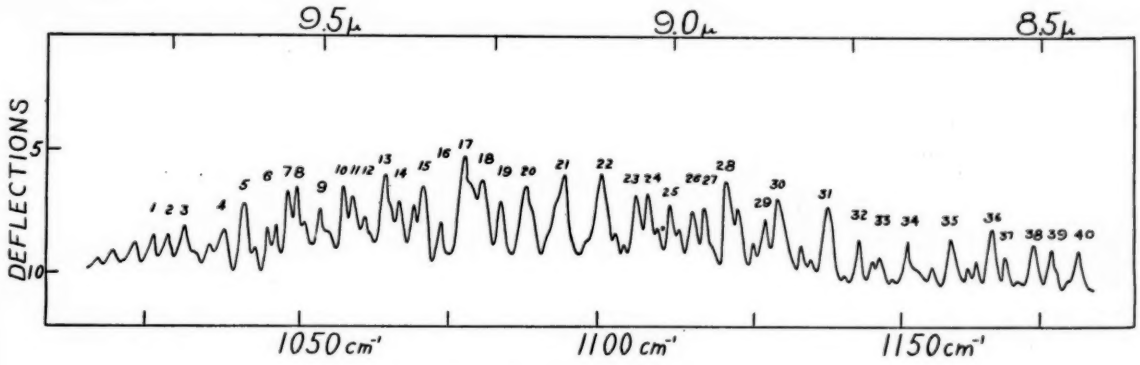

FIG. 1. The absorption in HDS at 9.0μ.

That at 3.1μ is undoubtedly the same observed by Bailey, Thompson and Hale[11] at 2.8μ. Our prism curve shows absorption from about 2.6μ to beyond 3.1μ, probably due to overlapping of the 2.7μ H_2S band with the region reported by Bailey, Thompson and Hale. Our prism instrument was, however, unable to resolve the two bands and we estimated that the part due to HDS was situated near 3.1μ. The value given by them is probably a more accurate one than ours. Due to the weakness of absorption, and the overlapping with the atmospheric water vapor fundamental it has not proved feasible to map this region under high dispersion. The region we reported at 4.1μ was due to an impurity in our gas. We have been able to demonstrate that the peak at 4.55μ reported in the spectrum of D_2S is actually due to the presence of a little CD_4[9] in our cell. This CD_4 was undoubtedly due to traces of Al_4C_3 occurring as an impurity in the Al_2S_3 which we used in preparing the D_2S. This 4.55μ region overlapping with the 3.8μ H_2S region gave the impression in our prism curve that there was a band at 4.1μ. Upon examination of this region with our grating instrument it became evident that there actually was no HDS band there. The 9.0μ band has been carefully measured, and the 3.8μ–3.9μ band reported by Bailey, Thompson and Hale investigated.

The 9.0μ region

The band reported by us at 9.0μ has been observed under high dispersion and is reproduced in Fig. 1. The curve is plotted in deflections of the galvanometer against a scale of frequencies in cm^{-1} and wave-lengths in μ. The deflections were read at intervals of 0.70 cm^{-1} with the spectrometer slits set to include a spectral interval of 0.8 cm^{-1}.

As may be seen from Fig. 1, the band is quite well resolved and shows a series of evenly spaced groups of lines, the average spacing of which is 6.85 cm^{-1}. This band contains no line or group of lines that can definitely be pointed to as a probable *Q* branch. Table I gives the frequency positions of the principal lines to which perfectly arbitrary numbers have been assigned. The center of this band we estimate to be at about 1090 cm^{-1}. A careful search was made to verify the strong line reported by Bailey, Thompson and Hale at 988 cm^{-1}, but it was not found. A fairly intense line was, however, located at 995 cm^{-1} which we have almost certainly identified as the *Q* branch of the low frequency fundamental of the CD_4 spectrum which occurs at exactly this point. We suggest that the line reported by the above authors at 988 cm^{-1} is probably the same one that we have found.

TABLE I. *Frequency positions of the lines in the HDS band at 9.0μ.*

Line No.	Frequency in cm^{-1}	Line No.	Frequency in cm^{-1}	Line No.	Frequency in cm^{-1}	Line No.	Frequency in cm^{-1}
1	1030.8	11	1068.0	21	1102.6	31	1147.1
2	1034.8	12	1071.7	22	1108.4	32	1152.0
3	1042.2	13	1074.3	23	1113.7	33	1156.2
4	1048.2	14	1076.6	24	1115.5	34	1160.9
5	1051.6	15	1080.4	25	1122.3	35	1169.4
6	1055.5	16	1084.0	26	1124.2	36	1174.9
7	1058.3	17	1087.0	27	1125.6	37	1178.1
8	1059.9	18	1090.4	28	1130.0	38	1182.9
9	1063.7	19	1093.7	29	1135.5	39	1186.2
10	1066.4	20	1096.6	30	1138.8	40	1191.8

[11] Bailey, Thompson and Hale, J. Chem. Phys. **4**, 625 (1936).

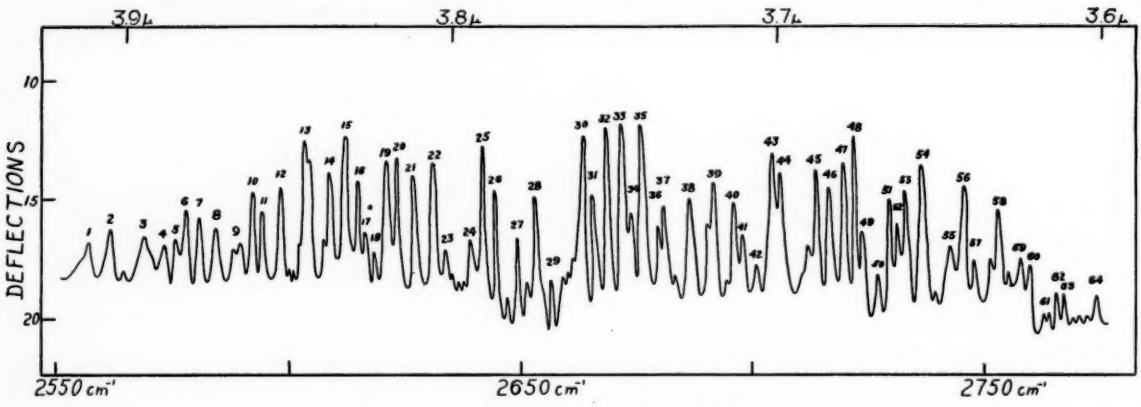

FIG. 2. The absorption band at 3.75μ in D_2S.

The 3.8μ region

This region, reported by Bailey, Thompson and Hale, we have carefully explored but we are unable to detect any absorption here by HDS although the lines of H_2S were observed. This would seem to indicate that this band is very faint since the gas we used was, as related above, a mixture of about 25 percent H_2S, 25 percent D_2S and 50 percent HDS.

D_2S

In our preliminary report we gave positions of bands in D_2S at 3.75μ, 4.55μ and 10.7μ. The 4.55μ band which we originally thought must correspond to the 3.8μ band in H_2S is, as we have already indicated, not due to D_2S but to the presence of a small quantity of CD_4 in our cell. Instead, Bailey, Thompson and Hale report a band at 1940 cm^{-1}. This band and the two others reported by us have been studied using a grating spectrometer.

TABLE II. *Frequency positions of the lines in the 3.75μ band of D_2S.*

Line No.	ν cm^{-1}	Line No.	ν cm^{-1}	Line No.	ν cm^{-1}
1	2559.3	22	2631.4	43	2704.4
2	2561.9	23	2634.1	44	2705.8
3	2568.8	24	2639.1	45	2713.6
4	2573.1	25	2641.9	46	2716.5
5	2575.3	26	2644.2	47	2719.9
6	2577.9	27	2649.2	48	2721.8
7	2581.0	28	2652.9	49	2723.8
8	2584.5	29	2656.6	50	2727.2
9	2589.8	30	2663.1	51	2729.4
10	2592.4	31	2665.5	52	2731.1
11	2594.2	32	2668.3	53	2732.6
12	2698.1	33	2671.6	54	2736.6
13	2603.0	34	2673.9	55	2743.0
14	2608.8	35	2675.8	56	2745.5
15	2612.4	36	2679.6	57	2748.0
16	2615.1	37	2681.0	58	2752.9
17	2616.4	38	2686.7	59	2756.9
18	2618.7	39	2691.4	60	2760.0
19	2621.4	40	2696.0	61	2763.0
20	2623.2	41	2697.2	62	2765.5
21	2626.8	42	2701.0	63	2767.0
				64	2774.6

The 3.75μ region

The shortest wave-length band observed in D_2S lies at 3.75μ and is shown in Fig. 2. The spectral region in which this band lies is quite free from atmospheric bands and galvanometer deflections were therefore plotted against a scale of frequencies in cm^{-1}, and wave-lengths in μ. The deflections were read at intervals of 0.90 cm^{-1} and the slit width included 0.70 cm^{-1}.

This band, the center of which appears to be about 2685 cm^{-1}, undoubtedly corresponds to the 2.6μ band in H_2S which, it will be recalled, has a somewhat broadened but unresolved Q branch. The band in D_2S also clearly shows a Q branch, but it is much broader than the one in the H_2S band and is seen to be partially resolved into a number of closely spaced components. The lines in the P and R branches are, of course, complex but a fairly uniform spacing taken between the centers of these groups is discernible and averaged over the band takes the value of 5.0 cm^{-1}.

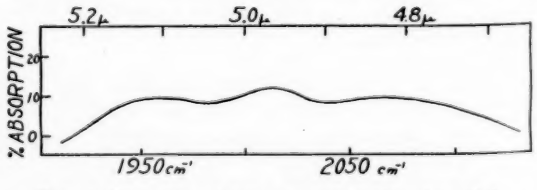

FIG. 3. Envelope of 5.0μ absorption band in D_2S.

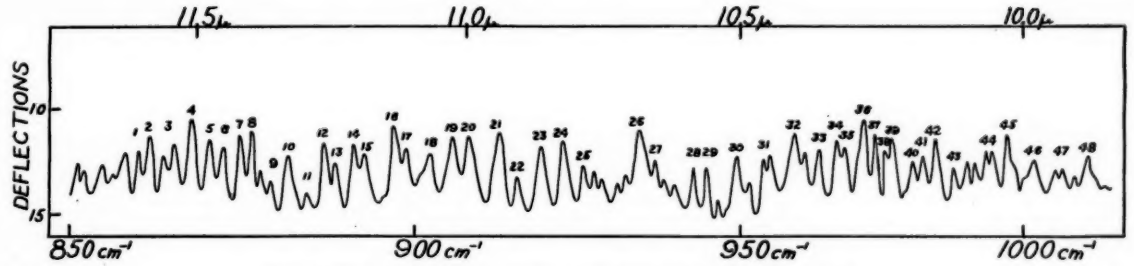

FIG. 4. The 10.7μ vibration-rotation band of D_2S in absorption.

Table II gives the frequency positions of 64 of the principal lines.

The 5.0μ region

This band, the center of which is given by Bailey, Thompson and Hale as 1940 cm^{-1} has been measured by us and an envelope of the band is shown in Fig. 3. The band, as suggested by these authors, undoubtedly corresponds to the 3.8μ band in H_2S. It occurs with fairly low intensity and already in this region there occur lines belonging to the 6.2μ water vapor band which are more intense than any lines in the D_2S band. These intense lines, we feel, are apt to have injected serious falsifications into the fine structure pattern and rendered it somewhat questionable in several places. For this reason we have not reproduced this fine structure but give only the envelope of the absorption region as is obtained when the spectrometer slits are widened. As may be seen, this envelope in general takes the shape predicted by Gerhard and Dennison for a perpendicular band of a molecule where $\beta=-\frac{1}{2}$.[12] As far as we have been able to discern there occurs no Q branch whatever in this region. The center of the band appears, from our measurements, to lie near 2000 cm^{-1} and in our fine structure pattern we were able to pick out many quite regular spacings of the order of 5.0 cm^{-1}.

The 10.7μ region

Fig. 4 shows the curve obtained for the D_2S band at 10.7μ. This band corresponds to the 8.0μ band of H_2S which was recently remeasured by Sprague and Nielsen and interpreted by them as one having a Q branch. The appearance of this band is quite similar to that of the corresponding H_2S band, in that it also contains a rather intense group of lines near the center which we are inclined to interpret as a diffuse and ill-defined Q branch. The rest of the band contains partially resolved multiplets which are fairly uniformly spaced with a $\Delta\nu$ of about 4.8 cm^{-1}.

Deflections were read at intervals of 0.50 cm^{-1} and the spectrometer slits were set to include a spectral region of 0.60 cm^{-1}. Since there was no atmospheric absorption in this region the curve was plotted in galvanometer deflections against a frequency scale in cm^{-1} and a wave-length scale in μ. Table III gives the frequency positions of 48 of the most intense lines in the band. As we have already pointed out, line 45 somewhat more intense than others nearby is almost certainly due to the Q branch of the long wave CD_4 band. The relative intensities of the other lines in the CD_4 band are much too small when compared with the Q branch, however, to contribute anything to the absorption pattern given in Fig. 4.

Interpretation of the observed data

The rotational analysis carried out by Cross on the band measured by him in the photographic infrared has enabled him to assign to the moments of inertia these values $I=2.667\times10^{-40}$ gcm^2, $I=3.076\times10^{-40}$ gcm^2 and $I=5.845\times10^{-40}$

TABLE III. *Frequencies of the lines in the 10.8μ band in D_2S.*

Line No.	ν cm^{-1}	Line No.	ν cm^{-1}	Line No.	ν cm^{-1}	Line No.	ν cm^{-1}
1	860.4	13	888.5	25	925.8	37	973.7
2	862.3	14	890.7	26	934.7	38	975.5
3	866.0	15	893.3	27	937.7	39	977.0
4	868.1	16	896.7	28	942.6	40	980.2
5	870.7	17	898.8	29	944.9	41	981.9
6	872.7	18	902.5	30	950.2	42	984.7
7	875.0	19	905.7	31	954.6	43	988.0
8	876.5	20	908.1	32	959.8	44	991.9
9	879.4	21	912.6	33	964.0	45	997.0
10	881.4	22	915.7	34	967.2	46	1000.4
11	884.6	23	919.3	35	968.8	47	1006.2
12	886.9	24	922.9	36	972.1		

[12] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

gcm². Assuming these values to be correct the H_2S molecule may be approximated by a symmetric model where two of the moments of inertia, say A and B, are alike and set equal to $\frac{1}{2}(I_A+I_B)$ and where the third moment of inertia $C=A+B$. In such an idealized model all three vibration frequencies ν_1, ν_2 and ν_3 would be perpendicular bands of identical appearance. They would consist of lines separated from each other by an interval $\Delta\nu=(h/8\pi^2A)$. In the actual case where I_A is only approximately equal to I_B this must also be essentially true except that the lines will split up into components certain of which will crowd toward the center of the band when the oscillation is along I_A giving the effect of a diffuse and a partly resolved Q branch; but these components will spread away from the center, leaving it bare, when the oscillation is along I_B. The spacings between what are now groups of closely spaced line components must, however, be very nearly the same in both types of vibration band. In fact, making use of the above values of I_A, I_B and I_C as computed by Cross to calculate what might be expected as the spacings between such line groups one finds a value in good agreement with those observed in the bolometric infrared bands. This has been interpreted by Sprague and Nielsen as confirmatory evidence that the values for I_A, I_B and I_C by Cross are at least of the right order of magnitude.

As indicated in the introduction two models of the H_2S molecule are possible, an obtuse model of vertex angle 92° 20′ and an acute model of vertex angle 85° which will satisfy the above values of the moments of inertia. Between these Cross was unable definitely to decide, but influenced by calculations made by himself and Van Vleck and by chemical evidence which definitely favors the obtuse model, he suggested the 92° 20′ vertex angle. The frequency 3970 cm^{-1} according to Nielsen and Barker and the frequencies 9911 cm^{-1} and 10,100 cm^{-1} according to Cross are all bands having Q branches and in conformity with his model are identified by Cross, respectively, as $\nu_2+\nu_3$, $3\nu_1+\nu_3$ and $3\nu_3+\nu_1$. This identification, it should be pointed out, gives no real verification for the obtuse model since on the basis of an acute model they might equally well be given the identification $\nu_1+\nu_2$, $2\nu_1+2\nu_3$ and $2\nu_2+3\nu_1$ as suggested by Sprague and Nielsen.

From a vibrational analysis of the bands reported in the spectra of H_2S, HDS and D_2S, Bailey, Thompson and Hale have arrived at a model for this molecule when the vertex angle is 110° a model in sympathy with evidence to be had from chemical sources. As we anticipated in the introduction, these bands alone do not suffice without further assumption to fix the shape of the molecule. This is especially true since from this work no knowledge is to be had concerning the rotational structure of the bands and hence in many cases their identification must have been made arbitrarily. Such a model would, moreover, be inconsistent with the rotational structure of the H_2S bands. For such a model as this nearly all semblance of regularity in rotational structure would have disappeared, certainly the spacings between line groups for the two types of bands could no longer be expected to be of the same magnitude. We are therefore inclined to feel that their value can hardly be regarded as numerically correct, but must be considered as giving only the order of magnitude of the angle.

As we have seen, however, by correctly identifying one of the fundamental bands and deciding upon the character of its rotational structure, we have a means of differentiating between the two models. Now the frequency at 1290 cm^{-1} in H_2S which must almost certainly be identified as ν_2 contains near the center a group of lines suggestive of the diffuse and ill-defined Q branch one might expect in a vibration along the axis of smallest moment of inertia. This fact has led Sprague and Nielsen to suggest that the correct model of the H_2S molecule is probably that where the vertex angle is 85°. Their view in this is supported by the fact that the region near 3.8μ does not resemble that at 8.0μ except insofar that the spacings between lines or line groups are the same. There is no evidence whatever of any piling together at the center of lines tending to form a Q branch; in fact this region resembles a perpendicular band in the spectrum of a symmetric molecule very much. They have, therefore, taken it to be ν_3, a vibration on the basis of their model along the intermediate moment of inertia. These same arguments are

valid in the case of D_2S. By analogy we should identify the frequency 934 cm^{-1} as ν_2 and the frequency 2000 cm^{-1} as ν_3. All the vibrations are in the plane of the molecule and if ν_2, as appears to be the case, has a Q branch it must be due to an oscillation of the electric moment along the axis of the smallest moment of inertia. Since, however, ν_2 is also an oscillation parallel to the symmetry axis of the molecule this must then be identified as the axis of the smallest moment of inertia. This condition would require the adoption of the acute model. In addition ν_3 does not appear to have a Q branch and it would therefore have to arise from an oscillation parallel to the axis of the intermediate moment of inertia. Since ν_3 is a vibration normal to the symmetry axis, the intermediate axis of inertia becomes identified with the normal to the bisector of the vertex angle.

The vibration ν_2 of the hybrid molecule HDS, which undoubtedly is the band lying near 9.0μ and the only one for which the rotational structure has been determined will have components of the electric moment lying along the axes of the smallest and the intermediate moment of inertia. Its appearance might therefore be expected to resemble a superposition of two bands, although not necessarily of the same intensity, one of ν_3 and another of the type ν_2 in the molecules H_2S and D_2S. The spacing between lines in these two types of superimposed bands should, on the assumption that H_2S, D_2S and HDS molecules are all nearly symmetric tops, however, still be nearly the same and one might well expect some regularity of spacing of the rotational lines as is here also apparent. It does not seem unreasonable, moreover, that any Q branch which one might anticipate finding here might very well be obscured because the band effectively may be resolved into two superimposed oscillations, respectively along two axes normal to each other.

TABLE IV.

	H_2S	HDS	D_2S
ν_1	2615 cm^{-1}	—	—
ν_2	1250 cm^{-1}	1090 cm^{-1}	934 cm^{-1}
ν_3	2685 cm^{-1}	—	2000 cm^{-1}
$\nu_1+\nu_2$ (85° model)	3790 cm^{-1}	—	2685 cm^{-1}
$\nu_3+\nu_2$ (92° model)			
Calculated spacings	9.5 cm^{-1}	6.7 cm^{-1}	4.9 cm^{-1}
Experimental "	9.0 cm^{-1}; 10 cm^{-1}	6.9 cm^{-1}	4.8 cm^{-1}; 5.0 cm^{-1}

Another kind of evidence favoring the acute H_2S molecule is obtained by noting that the Q branch in the band observed in the spectrum of D_2S at 3.8μ is much broader and more resolved than the Q branch in the corresponding band in the H_2S spectrum found at 2.7μ, a fact which one would interpret to mean that the parameter ρ defined by Dennison as the ratio of the smallest to the intermediate moment of inertia, is more nearly unity for D_2S than for H_2S. It is now a simple calculation to show that in order for this ratio to increase when the hydrogen atoms in the hydrogen sulfide molecule are replaced by deuterium atoms, the vertex angle must be less than 88° 16′. This argument is cited because it is entirely independent of any identification of the observed bands in terms of the normal vibrations of the molecule.

If for the moment of inertia of the H_2S molecule we take the values suggested by Sprague and Nielsen (which are virtually the same as those given by Cross) it is possible to compute the values of these also for HDS and D_2S. This we have done on the basis of a model with vertex angle 92° 20′ and one with vertex angle 85° 20′. For the two cases, the values obtained are the following: for HDS $I_A=3.9\times10^{-40}$ gcm^2 · $I_B=4.6\times10^{-40}$ gcm^2 and $I_C=8.5\times10^{-40}$ gcm and $I_A=4.0\times10^{-40}$ gcm^2, 4.4×10^{-40} gcm^2 and 8.4×10^{-40} gcm^2; for D_2S: $I_A=5.18\times10^{-40}$ gcm^2; 6.2×10^{-40} gcm and 11.4×10^{-40} gcm^2 and $I_A=5.4\times10^{-40}$ gcm^2; 5.7×10^{-40} gcm^2 and 11.1×10^{-40} gcm^2. Assuming that the values I_A and I_B are nearly enough alike so that we may approximate the rotational motion of the H_2S molecule by that of a symmetric rotator, we may calculate what the spacing between lines might be expected to be. The predicted values are compared with the actual experimental values in Table IV when also our identifications of the observed bands are given:

The conclusions to be derived from these data may briefly be summarized by stating that the rotational structure of the bands seems to indicate moments of inertia satisfied by one of the two models for the H_2S molecule when the vertex angles are 92° 20′ and 85° 20′. We are inclined to feel that the evidence is in favor of the latter model but the ultimate decision between the two can only be made after a complete rotational analysis of the bands has been carried out.

The Infrared Absorption of Various Solutions of Acetic Acid

WALTER GORDY*
Department of Physics, University of North Carolina, Chapel Hill, N. C.
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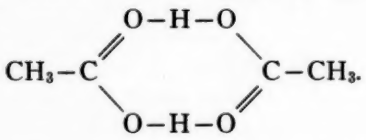
The characteristic vibrational band associated with the C=O group of acetic acid has been studied as a function of concentration of acetic acid in benzene, in carbon tetrachloride, and in isopropyl ether. The effects of benzene and carbon tetrachloride on the band were approximately the same. In both solvents the band became sharper, its intensity was increased, and its center was shifted to the longer wave-lengths. For concentrations of acetic acid as low as 6 percent the shift amounted to 0.15μ. Although in isopropyl ether solution there was a measurable shift of the band to the longer wave-lengths, the shift was small compared to that observed for benzene and carbon tetrachloride solutions. It is suggested that the changes in the C=O acetic acid band are likely due to variations in the polymerization of the acetic acid as the concentration is varied. However, the position of the band does not approach that for the vapor state in any of these solvents. Ethyl acetate was also studied in benzene and in isopropyl ether; no shifts could be detected in the C=O band.

CHEMICAL data[1] indicate that acetic acid in dilute solutions in benzene has a molecular weight equal approximately to that which it would have if polymerized into double molecules. In ether solution, however, acetic acid is thought to exist as double and as single molecules. Latimer and Rodebush[2] were the first to suggest that the association of acetic acid is due to the formation of hydrogen bonds. This theory has more recently been confirmed by other workers.[3] X-ray studies[4] support the theory that the acetic acid molecules are joined end to end through their carboxyl groups. It is thought that two molecules of the acid are joined by a pair of hydrogen bonds to form the monoplaner ring



If the acetic acid molecules are joined in this manner by hydrogen bonds, the infrared band associated with the C=O group would be affected and it should be possible to detect any changes in the association of the acid through measurements of this band.

In the present work a study has been made of the vibrational band of the C=O group of acetic acid as the concentration is varied in benzene, carbon tetrachloride, and isopropyl ether. For purposes of comparison a similar study was made of the C=O group of ethyl acetate for the same concentrations of ethyl acetate in benzene and in isopropyl ether. Transmission curves of pure acetic acid, of pure benzene, and of several solutions of different concentrations of acetic acid in benzene are shown in Fig. 1. The center of the C=O band in the pure acetic acid curve appears at 5.75μ. In benzene solution the band is slightly sharpened and is shifted to the longer wave-lengths. In the curve for 3 percent acetic acid the center of the band appears at 5.9μ. In addition, the intensity of the band is in-

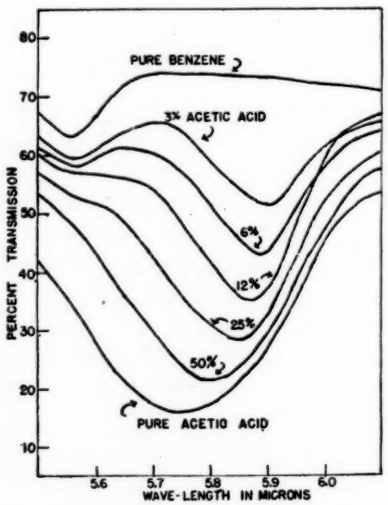


FIG. 1. Percentage transmission of acetic acid, of benzene, and of some acetic acid-benzene mixtures.

* Now at Mary Hardin-Baylor College.
[1] C. P. Smith, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, New York, 1931) p. 173.
[2] W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. **42**, 1419 (1920).
[3] Pauling and Brockway, Proc. Nat. Acad. Sci. **20**, 336 (1934).
[4] R. M. Morrow, Phys. Rev. **31**, 10 (1928).

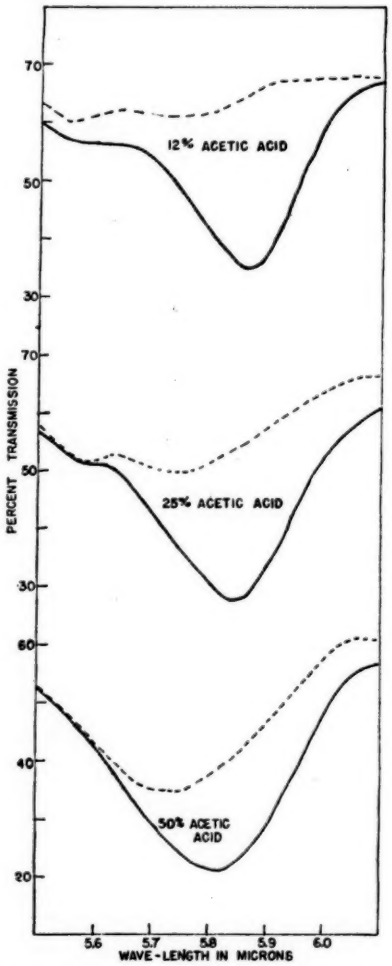


FIG. 2. Theoretical (dotted line) and experimental (solid line) transmission of acetic acid-benzene mixtures.

creased. It is advantageous to compare the transmission observed for some of these mixtures with that which would be expected if no chemical change should take place in either of the liquids and if neither component should influence in any way the spectrum of the other. Theoretical curves have been computed on the assumption that the absorption coefficient for the mixture at a given frequency is equal to a suitably weighed mean of the absorption coefficients of pure benzene and of pure acetic acid for the same frequency. These are compared with the experimental curves in Fig. 2. The method used in computing the theoretical curves has been given in a previous paper.[5] It is interesting to note

[5] Walter Gordy, Phys. Rev. **50**, 1151 (1936).

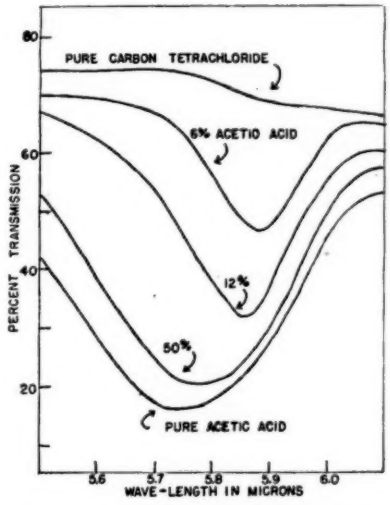


FIG. 3. Percentage transmission of acetic acid, of carbon tetrachloride, and of some acetic acid-carbon tetrachloride mixtures.

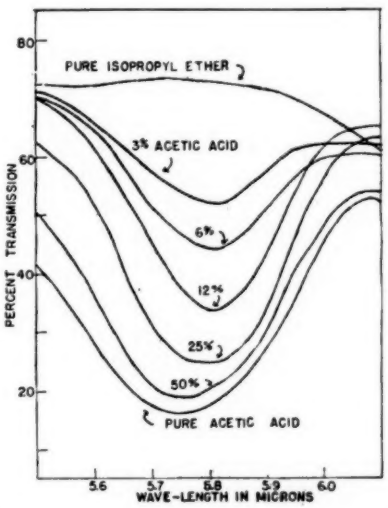


FIG. 4. Percentage transmission of acetic acid, of isopropyl ether, and of some acetic acid-isopropyl ether mixtures.

that the variations in the C=O band are very much the same when the solvent is carbon tetrachloride as when the acid is dissolved in benzene. This will be made evident by a comparison of the transmission curves for the same concentrations of acetic acid in these two solvents, Figs. 1 and 3.

If, as is generally believed,[1] acetic acid in ether solution exists in both dimeric and monomeric forms, one would expect the variations in the C=O band when the acetic acid is dissolved in ether to differ markedly from the variations of

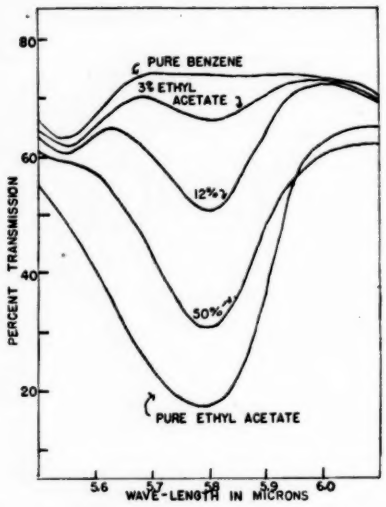


FIG. 5. Percentage transmission of ethyl acetate, of benzene, and of some ethyl acetate-benzene mixtures.

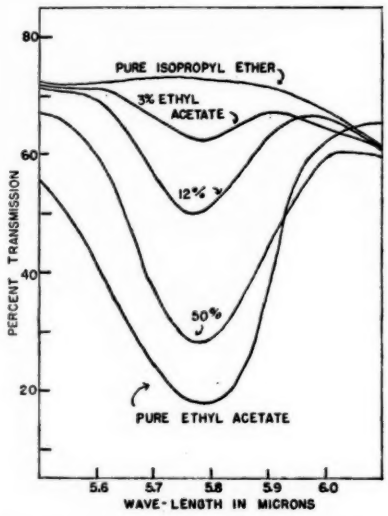


FIG. 6. Percentage transmission of ethyl acetate, of isopropyl ether, and of some ethyl acetate-isopropyl ether mixtures.

this band when the solvent is benzene, since in benzene, even in very dilute solutions, the acetic acid molecules are thought to be dimeric. Fig. 4 shows the effects of the isopropyl ether on the C=O acetic acid band. Although there is a shift to the longer wave-lengths, the shift is not as great as is the shift for acetic acid in benzene and in carbon tetrachloride. Furthermore, the band is broader for the lower concentrations in ether solution.

The shifts and marked intensity changes observed in the vibrational band of the carbonyl group of acetic acid when the acid is dissolved in benzene and in isopropyl ether apparently are not produced by these solvents upon the carbonyl band of ethyl acetate. There appears to be, nevertheless, a slight increase in the intensity of the band. Transmission curves showing the C=O ethyl acetate band and the effects of benzene and isopropyl ether on this band are given in Figs. 5 and 6. In Fig. 7 is given a comparison of the observed curves for two different ethyl acetate-benzene mixtures with the theoretical curves for the same mixtures.

The hydroxyl group not being present in ethyl acetate, it would not be possible for this substance to be polymerized through the formation of hydrogen bonds, as is acetic acid. Since the shifts of the C=O band in solutions of acetic acid were not observed for solutions of ethyl acetate, it seems likely that the shifts in the acetic acid band are due to variations in the association process. The shifts, being to the longer wave-lengths, do not indicate the formation of vapor-like molecules as has been reported for water and alcohol in nonpolar solvents.[6] Gillette and Daniels[7] obtained a shift of the C=O acetic acid band to the shorter wave-lengths as the acid was made to approach the vapor state

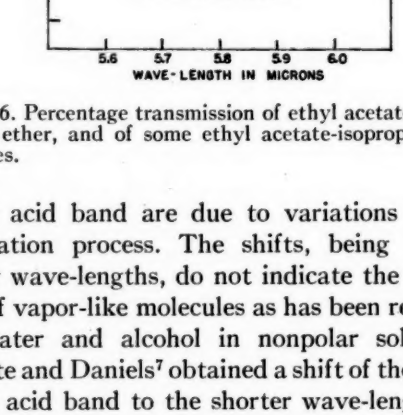


FIG. 7. Theoretical (dotted line) and experimental (solid line) transmission of ethyl acetate-benzene mixtures.

[6] E. L. Kinsey and J. W. Ellis, Phys. Rev. **49**, 105 (1936).
[7] R. H. Gillette and F. Daniels, J. Am. Chem. Soc. **58**, 1139 (1936).

through an increase of temperature. At a temperature of 172°C, at which, under the conditions of their experiment, the molecules were thought to exist principally as monomers, these observers reported the frequency of the band to be 1786 cm^{-1}. This frequency corresponds to a wavelength of 5.6μ. In the present work, it will be recalled, the position of the band was found to be 5.75μ for the pure liquid and 5.9μ for dilute solutions of the acid in benzene and in carbon tetrachloride. If, as is generally believed, the molecules exist principally as dimers in the dilute solutions, the difference in position and appearance of the band in the more concentrated solutions and in the pure liquid acid may indicate the presence of a more complex form.

The writer wishes to express his gratitude to Dr. E. K. Plyler for the use of his laboratory facilities and to Dr. B. G. Carson for his helpful suggestions.

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The Raman Spectra of Deuteroparaldehyde and Paraldehyde

R. W. Wood
Johns Hopkins University, Baltimore, Maryland
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RAMAN spectra of deuteroparaldehyde were obtained with material prepared by Professor E. Zanetti of Columbia University. A little over 1 cc was available sealed in a quartz tube furnished with a ground and polished window. As it seemed advisable to have spectra of ordinary paraldehyde made with the same instrumental equipment, a very pure sample was prepared and distilled into a tube of Pyrex glass of the same type. This was of some importance, as there is not complete agreement between the values obtained by Petrikaln and Hochberg, Venkateswaran and Bhagavantam and others.

The technique which I now employ in making spectrograms of the Raman effect differs from that which I have previously described, and is very superior in many ways. The same apparatus can be used for large or very small quantities of fluid, requires no auxiliary cooling devices, and enables one to excite the radiation either by the total light of the quartz mercury arc, or by 4358 or 4046 alone. A Hanovia mercury arc in its metal housing is turned on its trunnions into the vertical position, and a glass tube, 5 cm in diameter and 50 cm high (closed at the bottom) is mounted about 6 cm in front of the vertical aperture through which the light of the arc emerges. This tube is half-filled with water or an absorbing solution, and serves both as a cylindrical lens and ray filter. It is closed at the top with a cork to prevent evaporation, the vapor condensing on the wall and running down. The liquid under observation is contained in a tube of the form which I have previously described in numerous papers, shown in Fig. 1.

This is mounted in such a position that the mercury arc is focused along its axis, and a concave cylindrical mirror of thin and highly polished aluminum (now obtainable commercially) is attached to the rear wall as shown. The light emerging from the window at the bottom is reflected by a right angle prism and focused on the slit of the spectrograph by an achromatic lens of about 20 cm focus mounted at a distance of 2 meters from the prism. This arrangement insures that all parts of the illuminated column of liquid are in good focus, and no light scattered by the wall of the tube enters the spectrograph. The reflecting prism is held between two stiff brass clips, and can be rocked in the vertical plane or rotated on a vertical axis into such a position that the reflected image of the illuminated fluid column is exactly horizontal and in line with the axis of the collimator of the spectrograph. In some cases a flat tube filled with a strong solution of praeseodymium is inserted between the large tube and the irradiation tube. A certain brand of tooth brush is supplied in a

flat tube of soft glass suitable for the purpose. The tube can be drawn down, filled and sealed. This filter is of use for suppressing certain parts of the continuous spectrum of the mercury arc between the lines 4358 and 4916.

Adjustments are made as follows: A "pea" electric lamp, or other small source of light is mounted in front of and close to the center of the face of the prism, and the spectrograph pointed in such a direction that the image of the flame appears at the center of the camera lens, when the eye is placed at its focus, i.e. in the spectrum. The achromatic lens is now put in place and the image of the lamp focused on the slit, giving an approximate adjustment. A convenient way of getting a comparison spectrum both above and below the Raman spectrum is to saw a notch in a small right angle prism as shown by inset at bottom of Fig. 1, and mount this against the slit in such a position as to reflect the light of an iron arc to the slit, while the image of the Raman tube is transmitted through the notch.

To make sure that no light scattered from the walls of the tube enters the slit, proceed as follows: Start the mercury arc and open the slit about 1 mm. Adjust the achromatic lens so as to bring the image of the center of the circular ring of light scattered by the wall of the tube into coincidence with the notch on the prism.

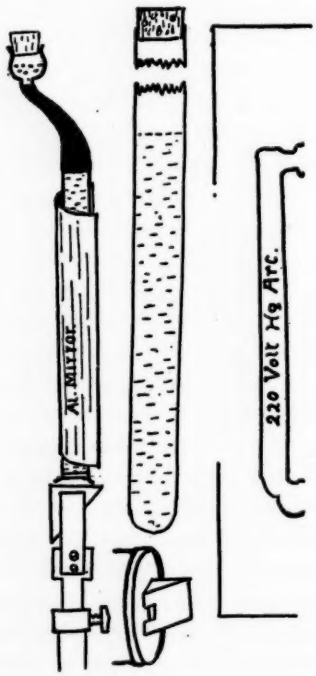

FIG. 1.

Examining the green mercury line with a short focus lens we shall then see the portion of the image of the "end-on" Raman tube that is transmitted through the notch, and can distinguish easily any portion of the relatively brilliant wall-image that gets through the slit. The lens is then to be slightly shifted until no part of the wall of the tube can be seen, or until the center of the image of the tube's cross section is coincident with the edge of the slit that remains fixed as the slit is closed. With a Raman tube of very small bore the ring of light may be wholly transmitted by the notch. In this case we shall have to be satisfied with a spectrum in which a horizontal strip along the middle is free from scattered light. This strip will be bordered above and below by the continuous spectrum of the arc.

The quartz tube containing the deuteroparaldehyde was about 6 mm in diameter and 25 cm long, with a liquid column at the bottom 5 cm high. The empty portion of the tube was wrapped with black tape, and there was no bend at the top. A small amount of light is reflected from the meniscus, but not enough to give serious trouble.

A spectrogram excited by the 4358 mercury line is reproduced in Fig. 2a. (Fe comparison.) The liquid used for the cylindrical condenser was a saturated solution of sodium nitrite, which absorbs all of the radiations of shorter wavelength. The $\Delta\nu$ values are given in Table I, each line numbered to correspond with the numbers on the photograph. The relative intensities of these lines can be seen from the spectrogram.

Spectrograms of paraldehyde were made with a much larger tube of Pyrex glass as shown in Fig. 1. The one made with 4358 excitation is reproduced in Fig. 2b. The spectrum excited by the total radiation was also photographed, as a control. Many lines not listed by previous investigators were found, twenty-three in all, against ten listed by Kohlrausch, two of which (900 and 1020) are nonexistent. The values are given in Table II.

We must now account for the discrepancies between the present values and those given by

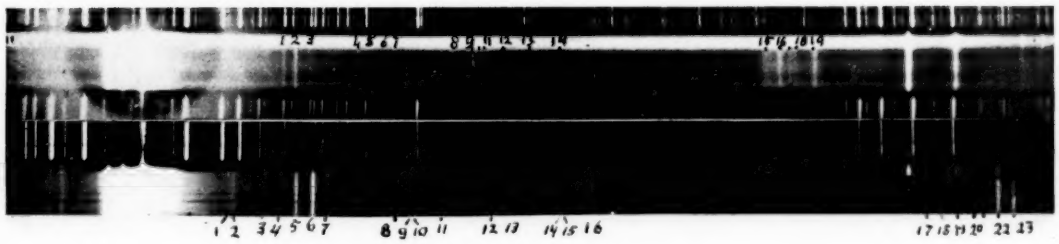

FIG. 2.

previous observers and listed in Kohlrausch's book on the Raman effect.

Petriakin gives a line 1015 and Vankateschar one at 1025. Kohlrausch gives the mean —1020. Both authors attribute this line to a line $\lambda = 4562$ excited by Hg 4358. Now there is *no* line 4562 by pure 4358 excitation. (If present it would come half-way between lines 10 and 11 in Fig. 2b.) It shows up, however, by excitation by the total radiation, and attributing it to 4046, we get $\Delta\nu = 2782$.

With 4358 excitation the corresponding Raman line would coincide with the mercury line 4960 and would hence be missed. It seemed worthwhile to look for this line and another spectrogram was made on a special plate sensitized for this region of the spectrum. A gelatine filter strongly dyed with ethylviolet was interposed between the sodium nitrite tube and the Raman tube. In this way the mercury lines 4915 and 4960 were eliminated from the esciting radiation. The result is shown at the right of Fig. 2b, this small region of the spectrum being pasted over the other (which shows as a narrow strip at the top, the two strongest lines to the left being 4915 and 4960). It is clear from the relative intensities that the latter line could not possibly register, as 4915 is quite faint, yet there is a clearly recorded line at this point in the original negative (line 19) giving a value of 2782 as required. This brands the line 1020 as spurious. Venkateschar and Bhagavantam record also a line 900, given by attributing $\lambda = 4536$ to 4358 excitation. I find a line at 4536 only with 4046 excitation, giving $\Delta\nu = 2665$, while with 4358 excitation we find a very faint line (No. 17) giving $\Delta\nu = 2660$. This disposes of the 900 line.

Their value $\Delta\nu = 845$ is the mean of the two clearly resolved lines 9 and 10 in Fig. 2, and their line 1178 corresponds to the middle of the broad band with sharp edges (No. 13, Fig. 2b) which is perhaps an unresolved triplet.

TABLE I.

No.	$\Delta\nu$	No.	$\Delta\nu$	No.	$\Delta\nu$
1	428	7	794	13	1262
2	470	8	981	14	1348
3	518	9	1043	15	2072
4	671	10	1063	16	2119
5	711	11	1077	17	2158
6	751	12	1144	18	2176
				19	2251

TABLE II.

	Wood	P.H.	V.B.		Wood	P.H.	V.B.
1.	258			11.	944	1015	1025
2.	274	276		12.	1108		1105
?3.	371			*13.	1162		
4.	424				1196		1178
5.	470	474	472	14.	1341		1350
6.	525	526	525	15.	1370		
7.	575		735	16.	1450	1452	1455
?8.	754		776	17.	2660		
9.	837	838	840	18.	2734		
10.	857		900	19.	2782		
				20.	2843	2863	2850
				†21.	2882		
				22.	2940	2942	2945
				23.	3000	3002	3000

* 13 is probably an unresolved triple line. Values given for the two edges.

† Probably excited by Hg 4347, i.e. to be excluded.

The Emission of Visible Light from Cavitated Liquids

LESLIE A. CHAMBERS
Johnson Foundation for Medical Physics and Department of Pediatrics, University of Pennsylvania
(Received February 6, 1937)

Emission of visible light from a number (14) of pure liquids and from some aqueous and non-aqueous solutions occurs during cavitation by intense sound waves of 8900 c.p.s. The intensity of the visible components of the radiation varies directly with the numerical product of viscosity (in poise) and dipole moment (in Debye units) and inversely with the temperature. In the case of polar solutes in nonpolar solvents the intensity varies with the concentration of the dipole. The light originates in cavitated areas or at the surface of the cavities, and is therefore proportional to the amount of cavitation, and in consequence, to the acoustic power input.

CERTAIN pure liquids emit visible light when cavitated by intense sound waves of audible frequency. The phenomenon was first recognized during the course of an experiment in which it was found that pure water, while sonically agitated, caused blackening of a photographic emulsion. A glow easily perceived by the dark adapted eye issued from the most vigorously cavitated regions in the body of the liquid.

Two similar observations involving ultrasonic frequencies, rather than audible, have appeared recently. Zimakov[1] has reported luminescence from certain aqueous solutions. It is his opinion that the phenomenon results from an electrical discharge between water vapor cavities and the glass walls of the containing vessel. Aqueous solutions of dichloroethanol, dichloroethane, NaI, NaCl, NH_4CNS and $Al_2(SO_4)_3$ were reported by Zimakov to emit light, while pure water and solutions of KI, acetic acid, and ethyl acetate did not.

On the other hand Frenzel and Schultes[2] observed a glow from pure water during ultrasonic treatment. They found that no light was emitted from degassed water and from this concluded that the light results from friction between cavitated gas bubbles and the water itself.

In the present communication some results of an investigation undertaken to determine the nature of the emitted light and the conditions necessary for its production are presented.

[1] P. V. Zimakov, Compt. rendus Acad. Sci. U. S. S. R. **3**, 450 (1934).
[2] J. Frenzel and H. Schultes, Zeits. f. physik. Chemie **27**, 421 (1934).

APPARATUS AND METHOD

The source of intense audible sound (8900 c.p.s.) used in the experiments was the modified Pierce magnetostriction oscillator previously described by Gaines[3] and by Chambers and Gaines.[4]

For each experiment 50 ml of the substance or solution was placed in a cylindrical glass vessel surrounding the nickel vibrator. The dimensions of the vessel were such that the end of the active element was about 3 cm below the liquid surface.

The temperature of the liquid was adjusted previous to placing it in the reaction vessel, and accumulation of heat through sound absorption was prevented by internal water cooling of the nickel vibrator. The latter precaution was unnecessary, however, since the emission of light, when it occurred, could be detected immediately upon the beginning of vibration and before any appreciable temperature rise.

In all cases the oscillator was operated at resonance for maximum acoustic energy output. Thus the conditions of treatment were, as nearly as possible, the same for all the liquids insofar as temperature and energy input were concerned.

Emission of light was detected by visual examination after dark adaptation of the operator for 30 minutes. This qualitative method permitted determination of the emission, or lack of emission, of light sufficiently intense to produce an effect on the retina. Furthermore, it was possible to estimate roughly the relative intensities emitted from the liquids examined.

[3] Newton Gaines, Physics, **3**, 209 (1932).
[4] L. A. Chambers and Newton Gaines, J. Cell. and Comp. Physiol. **1**, 451 (1932).

Experimental Results

Luminescence has been observed in the following liquids during sonic cavitation (arranged in order of relative light intensity):

1. Glycerol
2. Nitrobenzol
3. Ethylene glycol
4. *o*-Nitrotoluol
5. Isoamyl alcohol
6. *n*-Butyl phthalate
7. Dimethyl phthalate
8. Dibutyl phthalate
9. Water
10. *n*-Butyl alcohol
11. Corn oil
12. Propyl alcohol
13. Isopropyl alcohol
14. Ethyl alcohol

The emission from glycerol and nitrobenzol was visible without any dark adaptation, while the light produced in ethyl alcohol was so feeble as to be barely perceptible under the most favorable conditions.

On the other hand the following liquids showed no visible luminescence under the same conditions:

CCl_4	Ethyl acetate	Methyl alcohol
CS_2	Methyl acetate	Acetaldehyde
m-Xylol	Acetone	Amyl acetate
Benzol	Ethyl butyl acetate	Methyl salicylate
Toluol	Ethyl amyl acetate	Mesitylene
Ethyl ether	*n*-Tetradecane	Oleic acid
$CHCl_3$	Aniline	Cotton seed oil
		Chlorobenzol

An interesting empirical correlation between certain physical constants of the liquids and the relative intensity of visible light emitted has been found. It is that the apparent intensity is directly related to the numerical product of the viscosity (in 100 poise) and the molecular dipole moment (in Debye units) of the substance concerned. Table I illustrates this correlation insofar as reliable measurements of viscosity (η) and moment (μ) are available.[5]

Table I.

Substance	100η	μ	$\eta\mu$	Visible Emission (Relative)
Nitrobenzol	$2.013^{(20°)}$	3.90	7.85	+++++
o-Nitrotoluol	2. (est.)	3.75	7.5	+++++
Isoamyl alcohol	3.865	1.85	7.15	++++
Water	1.005	1.87	1.88	+++
n-Butyl alcohol	$2.8^{(22°)}$	1.74	4.87	+++
Propyl alcohol	$2.23^{(20°)}$	1.66	3.70	++
Isopropyl alcohol	1.95	1.78	3.47	++
Ethyl alcohol	$1.192^{(20°)}$	1.63	1.94	+
Chlorobenzol	0.751	1.52	1.14	0
Methyl alcohol	$0.591^{(20°)}$	1.64	0.97	0
Acetone	0.3	2.70	0.81	0
Methyl acetate	$0.478^{(0°)}$	1.67	0.80	0
Ethyl acetate	$0.44^{(20°)}$	1.74	0.77	0
Chloroform	$0.564^{(20°)}$	1.10	0.62	0
Acetaldehyde	0.223	2.68	0.60	0
Ethyl ether	0.226	1.22	0.28	0
Toluol	0.552	0.52	0.29	0
Benzol	$0.649^{(20°)}$	0.06	0.04	0
m-Xylol	0.595	0.06	0.04	0
Carbon disulphide	$0.367^{(20°)}$	0.06	0.02	0
Carbon tetrachloride	$0.96^{(20°)}$	0.00	0.00	0

All values of η are at 25° except as noted.

Water seems to be the only exception thus far encountered to the general rule that the intensity of visible emission is related to the product ($\mu\eta$). However, it should be pointed out that the dipole moment given for water is from data involving only the vapor state.

We may conclude from the data of Table I that there is in no case an emission of light of sufficient strength to affect the retina when the product ($\mu\eta$) falls below a limiting value. The emission from ethyl alcohol ($\mu\eta = 1.94$) was so feeble as to be barely detectable after 30 minutes of dark adaptation.

Two groups of correlative data have resulted from experiments on a series of liquids for which one or the other of the two variables (μ and η) was the same. In each case the relative intensity of visible radiation was found to be proportional to the free variable thus lending credence to the apparent correlation already drawn.

First, it is possible to select a series of substances in which the dipole moments are of the same magnitude while the viscosities differ.

Table II.

	μ	100η	$\mu\eta$	Relative Light Intensity
Methyl	1.64	0.591	0.97	0
Ethyl	1.64	1.192	1.94	+
n-Propyl	1.66	2.23	3.70	++
Isopropyl	1.78	1.95	3.47	++
n-Butyl	1.74	2.801	4.87	+++
Isoamyl	1.85	3.863	7.15	++++

Table III.

	μ	100η	$\mu\eta$	Relative Light Intensity	
ortho	6.05	(0.649)	3.93	Bright	+++
meta	3.81	(0.649)	2.47	Very feeble	++
para	0.32	(0.649)	0.21	None	0

[5] *International Critical Tables* and Trans. Faraday Soc. (1934).

TABLE IV.

% Nitrobenzol	Relative light emission (at 28°)	Variation of relative emission with temperature
100	Very bright	Somewhat dimmed at 63°
80	Bright	Somewhat dimmed at 57°
60	Less bright	Dim at 55°
40	Dim	Barely perceptible at 52°
20	Very dim	No light at 52°
0	None	

Such a situation occurs in the homologous primary alcohols indicated in Table II.

With essentially equal moments the emission is proportional to the viscosity, there being graded increase in light intensity from ethyl to isoamyl alcohol, methyl emitting none.

Again, it should be possible to select a series of fluids of essentially equal viscosity but which differ in respect to electric moment. This has proved difficult in the case of pure liquid substances. However, the three dinitrobenzols in benzol solutions of approximately equal viscosity illustrate the principle shown in Table III.

Each test sample consisted in a one-half percent solution of the indicated dinitrobenzol in C. P. benzol. The value taken for viscosity in the table is that of benzol since the addition of the derivatives in such low concentration did not greatly alter the value. In this case with similar viscosities the apparent brightness varied with the moment.

Since viscosity decreases with rise in temperature experiments were devised to determine the relation of the emission intensity to temperature of the substance. In the case of dibutyl phthalate the light was quite bright during vibration at 25°. The cooling arrangement was disconnected so that the liquid rose to 70° in four minutes. As the temperature increased the light intensity gradually decreased until no emission was visible. The liquid was then cooled to 25° whereupon vibration caused luminescence of about the same intensity as at the start of the experiment. Dimethyl phthalate behaved in a similar manner. In the case of glycerol the vibration was continued for 10 minutes without cooling, and the emission of light was never completely inhibited although its intensity was markedly diminished at the final temperature of 80°. The emission was of normal brightness when the liquid was recooled to the starting temperature (25°). A similar behavior has been noted in all the liquids previously observed to emit light at 25°.

In the case of solutions of polar compounds in nonpolar solvents, there should, under the implications of the empirical rule set forth above, be a relation between the intensity of the emitted light and the concentration of the polar substance. A series of solutions of nitrobenzol in toluol was prepared and vibrated to determine whether or not such a relationship exists. Table IV shows the results of the experiment. It will be seen that the relative intensity in this case is, in fact, directly related to the concentration of polar molecules. The right-hand column of Table IV constitutes further confirmation of the temperature relationship indicated previously.

In addition to the experiments recorded above which relate the phenomenon of acoustic luminescence to certain physical constants of the various systems, direct observation during vibration has revealed some information as to the locale of the light production. No emission has been observed in any liquid in the absence of cavitation. Furthermore, the radiation seems to be localized exclusively at the surface of the cavities. Therefore, it appears brightest in the region immediately adjacent to the end of the vibrator, although not entirely confined to that region.

Two useful reference points are available for estimation of the absolute intensity of the emitted radiation although no quantitatively objective measurements have been made. The emission from ethyl alcohol seems to approach the threshold of human retinal sensitivity, while the brightest observed so far (from glycerol) will blacken a photographic plate (E. K. nitrate) in 4 minutes at a distance of 10 cm.

The duration of the luminescence depends only on the duration of the applied sonic field with exposure times up to ten minutes. There is no persistence or afterglow; all visible emission ceases at once with cessation of cavitation.

No analysis of the spectral characteristics of the radiant emission is available as yet. Obviously the correlations indicated by the data of this paper take into account only the visible components of the radiation, and may therefore require reconsideration if ultraviolet or infrared components are later found to be present.

Vibration Spectra and Molecular Structure

II. The Force Constants of the C−C and C−O Bonds in Organic Molecules[1]

LYMAN G. BONNER*
Palmer Physical Laboratory, Princeton University, Princeton, N. J.
(Received February 11, 1937)

Force constants are calculated from known vibration frequencies for several of the simpler organic molecules by an approximate method involving neglect of the interactions between motions of hydrogen atoms and other atoms. Frequency expressions are given for several special forms of the triatomic molecule, and the C−C and C−O force constants are calculated for ethane, propane, cyclopropane, ethylene oxide, ethyl alcohol, isobutane, dimethyl ether, and methyl alcohol. The values obtained are, in general, in the neighborhood of 3.8 and 4.5×10^5 dynes/cm, respectively.

AS was mentioned in I[2] of this series, a knowledge of the force constants of the various interatomic bonds existing within a molecule is frequently helpful in assigning the observed infrared absorption or Raman frequencies to specific bonds. The purpose of the present paper is to calculate the values of the C−C and C−O force constants in a number of the simpler organic molecules. Since these molecules are, in general, too complex to be treated by the usual more rigorous methods of vibration analysis, approximations must be introduced, and the agreement in the final values obtained will serve as a check on the degree of validity of these approximations.

For most of the molecules herein treated vibration frequency values were taken from Raman data in the literature. In two cases, however, these data were supplemented by experiments in this laboratory. Infrared absorption curves were obtained in the region 1–15μ for gaseous cyclopropane and ethylene oxide, and in addition a redetermination was made of the liquid ethylene oxide Raman spectrum. These experiments will be discussed in a paper to appear in the near future. The frequency values obtained will be given later when each molecule is considered in detail.

THE FORCE CONSTANT CALCULATIONS

The type of calculation to be made here was briefly outlined in I, but it may be to the point to give further details at this time. As was mentioned there, the principal simplification to be made is the neglect of the effect of hydrogen atom vibrations on the relatively slower motions of the heavier centers. Each carbon or oxygen atom, together with its attached hydrogens, will be considered as a rigid body of mass equal to that of the atom plus the hydrogens. In effect we are saying that the motions of the hydrogen atoms, which are light compared with all other atoms found in organic compounds, do not exert sufficient force on the atoms to which they are attached to affect appreciably their motions relative to other heavy atoms. Some justification for this view is found in the extreme constancy of the C−H stretching and bending frequencies in the regions of 3000 and 1400 cm^{-1} in all organic molecules. This view of the molecule results in a tremendous simplification of the problem of calculating interatomic force constants, and most of the molecules treated in this paper may be handled simply as triatomic cases.

The other main approximation will be the use of harmonic force potential functions in connection with observed vibration frequencies rather than with the so-called "mechanical" frequencies, or frequencies for infinitesimal amplitudes of oscillation. It is doubtful if the error introduced by this will be appreciable, however, since the anharmonicities will be small for vibrating bodies with masses as large as those handled in this paper.

The equations relating vibration frequencies and the various molecular constants in triatomic molecules have been published in the past, but

[1] Presented in part before the American Chemical Society, Pittsburgh, Sept. 1936.
* National Research Fellow.
[2] R. B. Barnes, L. G. Bonner and E. U. Condon, J. Chem. Phys. **4**, 772 (1936).

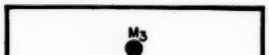

FIG. 1. Dimensions of the general triatomic molecule.

it is believed that, for certain special cases, these equations have been put in particularly simple form, and are worth giving at this time. We are concerned here only with nonlinear molecules, and the dimensions of the general triatomic molecule are given in Fig. 1. The equations for this asymmetric model, based on a potential function of the form

$$2V=k_1(\Delta r_1)^2+k_2(\Delta r_2)^2+k_3(r_1^{\circ 2}+r_2^{\circ 2})(\Delta\alpha)^2$$

have been given by Lechner,[3] and, in a more convenient form, by Cross and Van Vleck[4] and need not be repeated here. In solving the equations for this type of molecule it was found most convenient to assume values for the three k's, substitute these in the secular equation, solve for the three frequencies, and vary the values of the k's until the best fit with experiment was obtained. The secular equation is a cubic in λ, a quantity proportional to ν^2, and can be most readily handled by a graphical method suggested by Professor E. U. Condon. This method is perhaps interesting and useful enough to merit description. Starting with the general cubic in the form

$$x^3+ax^2+bx+c=0,$$

the substitution $x=Ay-a/3$ is made. If A is so chosen that

$$A^3=c-ab/3+2a^3/27$$

and the equation is divided through by A^3, the result is of the form $y^3-\alpha y+1=0$ where $\alpha=(a^2/3-b)/A^2$. Since now $\alpha=1/y+y^2$ a large scale plot of α against y may readily be constructed from which y, and hence x may be obtained to any desired accuracy for any given set of coefficients.

[3] F. Lechner, Monatsh. f. Chem. **61**, 385 (1932).
[4] P. C. Cross and J. H. Van Vleck, J. Chem. Phys. **1**, 350 (1933).

For the symmetrical triatomic model, with $m_1=m_2=m$, $m_3=M$, and $r_1^\circ=r_2^\circ$ the calculations are considerably simplified. Since $k_1=k_2$ we may include one interaction term in the potential function, and V takes the form

$$2V=k_1\{(\Delta r_1)^2+(\Delta r_2)^2\}+r_1^{\circ 2}k_3(\Delta\alpha)^2 +2k_{12}(\Delta r_1)(\Delta r_2).$$

The valence angle, α, appears in the equations as a fourth parameter, and it is frequently possible to determine this, in addition to the three k's, from the vibrational analysis. Since in many molecules α is practically independent of the small constant k_{12}, this may be taken as zero, and k_1 and k_3 eliminated from the frequency expressions leaving α as a function of the three frequencies. If we adopt the notation

$$\mu_1=\frac{m(M+m)}{M+2m}, \quad A=\mu_1-\mu_2\cos\alpha,$$

$$\mu_2=\frac{m^2}{M+2m}, \quad B=\mu_1+\mu_2\cos\alpha,$$

$$C=\mu_1^2-\mu_2^2,$$

and take the frequency equations given recently,[5] we have the expressions for the angle:

$$x^3-M\mu_2\lambda_1(\lambda_1+\lambda_2+\lambda_3)x/\lambda_2\lambda_3 +2M\mu_1\mu_2\lambda_1^2/\lambda_2\lambda_3=0, \quad (1)$$

$$\cos\alpha=1+M/m-x/\mu_2.$$

The k's may be calculated from the equations

$$k_1-k_{12}=C\lambda_1/A,$$

$$(k_1+k_{12})^2B/A-C(\lambda_2+\lambda_3)(k_1+k_{12})/A +C\lambda_2\lambda_3=0, \quad (2)$$

$$k_3=C(\lambda_2+\lambda_3)/2A-B(k_1+k_{12})/2A.$$

For this case λ_1 is the asymmetric stretching vibration, and λ_2 and λ_3 the symmetric stretching and deformation vibrations.

As was pointed out in part I it is very convenient to use k in units of 10^5 and m in atomic weight units. On this scale λ is related to $\tilde{\nu}$, the frequency in cm^{-1}, by the expression.

$$\lambda=5.851\times10^{-7}\tilde{\nu}^2.$$

All calculations in this paper will be carried out in these terms.

[5] L. G. Bonner, Phys. Rev. **46**, 458 (1934).

Another form of the symmetrical triatomic molecule is the cyclic model of which ethylene oxide is an example. Here a potential function of the central force type must be used since the principal restoring force no longer resides in the valence angle of the central atom, but results from the relatively much stronger chemical bond existing between atoms 1 and 2. If

$$2V=k_1\{(\Delta r_1)^2+(\Delta r_2)^2\}+k_3(\Delta r_3)^2 +2k_{12}(\Delta r_1)(\Delta r_2)+2k_{13}(\Delta r_3)\{(\Delta r_1)+(\Delta r_2)\}$$

we may, by the usual methods, derive the frequency expressions. They are:

$$\lambda_1=(k_1-k_{12})A/C,$$
$$\lambda_{2,3}=1/2C\{B(k_1+k_{12})+2(\mu_1-\mu_2)(k_3+k_{13}r_3/r_1)\} \pm 1/2C[\{B(k_1+k_{12})+2(\mu_1-\mu_2)(k_3+k_{13}r_3/r_1)\}^2 -4C(1+\cos\alpha)\{k_3(k_1+k_{12})-2k_{13}^2\}]^{\frac{1}{2}}. \quad (3)$$

A special case of Eqs. (3) will be the completely symmetrical cyclic model in which all three masses and distances are equal. As a result of the confluence of two vibration modes we have only two distinct vibrations and their frequencies are given by

$$\lambda_1=3(k_1-k_{12})/2m, \quad \lambda_2=3(k_1+2k_{12})/m. \quad (4)$$

The method of performing the calculation for a specific molecule consists simply of selecting, from the observed Raman and infrared data those frequencies attributable to the mutual vibrations of the C and O atoms and substituting the values in the appropriate ones of the above equations. Even in cases for which the number of observed frequencies is very large the problem of selecting the correct ones is not as difficult as it might at first sight appear. In the simple cases of ethane and methyl alcohol the C−C and C−O frequencies fall at 993 and 1030 cm^{-1}, respectively, and the great wealth of experimental evidence now existing strongly indicates that vibration frequencies for these bonds in other molecules will usually not be far different from the above values. Those frequencies for which the restoring force results solely from the stability of a valence angle are usually so low that they are readily picked out.

We may now proceed to the consideration of specific cases.

Results

Ethane

This simple type of molecule may be treated as diatomic and the force constant calculated from the relation $\lambda=k/\mu$. Using the well-known value 993 cm^{-1} for the frequency of the mutual oscillation of the two CH_3 groups, this yields a value (in units of 10^5 dynes/cm) $k=4.30$.

Propane

Using the Raman data of Bhagavantam[6] the only frequencies lying in the desired regions are 1055, 867, and 377 which must be, in order, ν_1, ν_2 and ν_3. Using first Eqs. (1) we find a valence angle of 117°, and putting this value, together with the frequencies, in (2) we obtain $k_1=3.84$, $k_{12}=0.045$ and $k_3=0.34$. It is to be noted that as a result of dynamical interaction between the two identical bonds to the central carbon atom, the single frequency of ethane is split into two, one above and one below the original frequency, and both of these must be considered characteristic of the C−C bond.

Cyclopropane

In this completely symmetrical model, as was mentioned above, two vibrations coalesce and we need search for only two frequencies characteristic of the ring. The most recent Raman measurements are by Harris, Ashdown, and Armstrong[7] and show strong frequencies in the region of interest at 869, 1022, and 1191 cm^{-1}. The infrared measurements made in this laboratory show absorptions at 861 and 1021 cm^{-1} only. According to the selection rules as given by Placzek[8] both the ring frequencies of cyclopropane should be active in the Raman but only one in the infrared. On this basis 1191 is certainly one of the frequencies, and taking 869 for the other we calculate from (4) $k_1=4.04$, $k_{12}=-0.084$.

Perhaps an even more reasonable choice of potential function for this molecule would be that in which the second term involves the angle deformation rather than the valence interaction.

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[6] Bhagavantam, Indian J. Phys. **6**, 595 (1932).
[7] Harris, Ashdown and Armstrong, J. Am. Chem. Soc. **58**, 852 (1936).
[8] In *The Structure of Molecules* (P. Debye, London, 1932).

The form of this would be

$$2V = a\sum(\Delta r_i)^2 + br_0^2\sum(\Delta\alpha_i)^2.$$

The transformation from the constants of Eq. (4) is readily made and we find $a=3.86$, $b=0.084$. This unusually small value of the deformation constant is not unreasonable when one considers the highly strained nature of the system. The normally tetrahedral angles at the carbon atom have been reduced to 60°. However, as will be shown below in the case of ethylene oxide, it is likely that this type of function is not as satisfactory for the valence bond constants as is that involving the bond interactions, and the values given first for k_1 and k_{12} will be used.

Ethylene oxide

Recent Raman work by Ananthakrishnan[9] shows lines, in the region of interest, at 807, 869, 1122, 1159, and 1270 cm^{-1}, with 1122 and 1159 weak, in good agreement with the Raman and infrared measurements made in this laboratory. Practically the only choice for the three frequencies is 869, 1270, and 807, and a trial calculation quickly shows that this is the correct order. The general quadratic potential function for this molecule, as given above, contains four constants, two of which represent interactions. As might be expected in this highly strained system the interactions are rather large and neither k_{12} nor k_{13} can be neglected. All that could be done in this case was to construct a plot, shown in Fig. 2, of k_1, k_3, and k_{12} against k_{13} as a parameter, for the three frequencies given above. Since the interaction between two like bonds is probably stronger than that for unlike bonds the point at $k_{13}=0.20$ was rather arbitrarily selected. The force constant values here were $k_1=4.43$, $k_3=3.73$, $k_{12}=0.33$, and $k_{13}=0.20$. As defined in the potential function above, k_1 is the constant for the C−O bond and k_3 for the C−C bond. A function similar to that introduced above for cyclopropane, involving two valence terms and two angle terms, may also be used. However, it is found, when the transformation is made, that there is no solution, over the whole range of reasonable valence constant values, which yields positive values for both angle

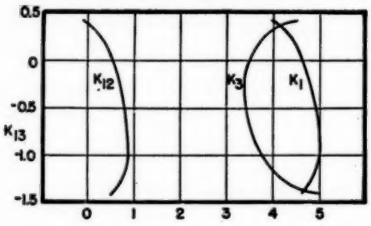

FIG. 2. k_1, k_3, and k_{12} plotted against k_{13}, for ethylene oxide.

constants. This result serves in part to demonstrate the crudity of the potential functions used, but perhaps also indicates that the solution involving interactions is a little more reliable.

Ethyl alcohol

According to Bolla,[10] this molecule shows, in the low frequency region, Raman lines at 257, 433, 814, 883, 1051, and 1096 cm^{-1}, with the 814 line very weak. Using the set 1051, 883, and 433 Cross and Van Vleck[4] obtained the values 3.6 and 4.1 for the C−C and C−O force constants. 4.1 is almost certainly too low, and a different choice of frequencies, in which 1096 is substituted for 1051 leads to the much more reasonable set of values $k_1=3.80$, $k_2=4.48$ and $k_3=0.23$. It is interesting to note that here, even though the two bonds to the central atom are different they are sufficiently alike both as to mass of attached group and as to bond force constant to interact appreciably. The C−C frequency is shifted to a lower and the C−O to a higher value than would normally be the case. The possibility of this interaction was first pointed out by Cross and Daniels.[11]

Isobutane

This molecule is of the ammonia type, and is the only one treated in this paper which is not, to the degree of approximation assumed, triatomic. The force constant equations for this molecular type have been derived recently by Howard and Wilson[12] and may be applied in the form given in their paper. The Raman spectrum as determined by Kohlrausch and Köppl,[13] shows

[9] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **4**, 82 (1936).

[10] Bolla, Zeits. f. Physik **90**, 607 (1934).

[11] P. C. Cross and F. Daniels, J. Chem. Phys. **1**, 48 (1933).

[12] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 10 (1934).

[13] Kohlrausch and Köppl, Zeits. f. physik. Chemie **26B**, 209 (1934).

TABLE I. *Summary of force constant calculations.*

MOLECULE	FORMULA	FREQUENCIES (cm^{-1})	FORCE CONSTANT C–C	FORCE CONSTANT C–O
Ethane	C_2H_6	993	4.30	
Propane	C_3H_8	377, 867, 1055	3.84	
Cyclopropane	C_3H_6	869, 1191	4.04	
Ethylene oxide	C_2H_4O	807, 869, 1270	3.73	4.43
Ethyl alcohol	C_2H_5OH	433, 883, 1096	3.80	4.48
Isobutane	C_4H_{10}	372, 436, 796, 1177	4.29	
Dimethyl ether	C_2H_6O	416, 930, 1102		4.56
Methyl alcohol	CH_3OH	1030		5.00

lines at 372, 436, 796, 967 and 1177 cm^{-1}. A little experimentation shows that the correct assignment, in the notation of Howard and Wilson, is $\nu_1=796$, $\nu_2=436$, $\nu_3=1177$ and $\nu_4=372$. Unfortunately the values calculated for the force constants are very sensitive to the valence angle assumed for the central carbon, and this angle has not, to date, been determined with any accuracy. Two values for the C–C force constant may be calculated from the two frequency sets ν_1, ν_2 and ν_3, ν_4, and the method finally devised was that of varying the angle until the two values coincided. This procedure led to the values 114° for the angle between adjacent C–C bonds, 4.29 for the stretching constant, and 0.48 for the deformation constant.

Dimethyl ether

This is a simple molecule calculable by application of Eqs. (1) and (2). Taking the frequencies (Dadieu and Kohlrausch[14]) as 1102, 930 and 416 we obtain 114° for the valence angle and the values $k_1=4.56$, $k_3=0.46$ and $k_{12}=-0.045$ for the force constants.

Methyl alcohol

Taking the well-known value 1030 for the frequency of the C–O vibration and the reduced mass of CH_3 and OH, we obtain $k=5.00$ for this molecule.

[14] Dadieu and Kohlrausch, Sitzber. Akad. Wiss. Wien 139, 459 (1930).

DISCUSSION

Table I gives a summary of the force constant calculations made in the previous section. It is to be noted that for both the C–C and C–O bonds the diatomic molecule approximations yield results some 10–12 percent higher than the triatomic ones. For the single pyramidal case, isobutane, the force constant is again near that of the diatomic molecule. It seems obvious that, making the approximation of neglecting the dynamic effects of the hydrogen atoms, the force constant value obtained for a specific bond will be considerably influenced by the exact shape of the molecule. Hydrogen vibrations will interact differently with those of the heavy atoms in molecules of different geometric configurations. Another source of discrepancy among force constant values calculated for the same bond in different molecules, one that is inherent in the customary normal coordinate method of treatment, lies in the fact that the potential functions used are rarely unique. Even for a simple molecule it is frequently possible to write the function in several ways each of which defines the main constants in slightly different manners. An example of this would be the valence and central force functions for a simple triatomic molecule. Under the circumstances, then, the agreement among the force constant values presented in Table I is perhaps as good as could be expected. It is unfortunate that there have not been made enough exact force constant calculations to make it possible either to follow the fluctuations under varying circumstances or to determine exactly the values of either of the two constants with which we are concerned in this paper. The author feels, in any case, that for molecules that may be treated as triatomic the apparent values of the C–C and C–O force constants are very near to 3.8 and 4.5, respectively, and that neither the true values nor the apparent values under most conditions will be different from the above by more than 10–15 percent.

The Effect of Radiation on Oil Drops

WILHELM STENSTROM AND IRWIN VIGNESS
Section of Biophysics, Medical School, University of Minnesota, Minneapolis, Minn.

(Received February 15, 1937)

Oil drops on a water surface increase their diameter when they are irradiated with β-rays, x-rays, or ultraviolet rays. The growth of the diameter depends on the amount of exposure to the radiation. Curves showing the increase of diameter with time have been made. If oil in a closed container is irradiated with x-rays, and drops from such irradiated oil are placed on a water surface, the drops spread and reach a limiting size after a few hours. The experiments made are of a preliminary nature and are intended to demonstrate the general nature of the phenomena.

THE behavior of oil on water has been studied by many investigators and articles by Langmuir[1] have stimulated us to undertake this study. When a small amount of fatty acid with a relatively long hydrocarbon chain is placed on a large water surface it spreads to form a monomolecular layer. The molecules are packed together side by side and become oriented so that they are approximately vertical, with the acid group in the water. A drop of long chain hydrocarbons, like petrolatum, on the other hand does not spread in a similar manner, but forms a lens that floats on the water. If one part of stearic acid is dissolved in about 20,000 parts of petrolatum, and a drop of this solution is placed on alkaline water, it gradually spreads and reaches a limiting size after a few minutes. According to Langmuir the area over which the drop spreads is proportional to the amount of stearic acid in the drop and independent of the amount of petrolatum, which indicates that all the stearic acid molecules go to the interface where each molecule contributes a certain size to the area. When a small amount of hydrocarbon in an open container is partially oxidized, for instance by heating, and a drop of this oil is placed on the water, it spreads in a similar manner. It seemed probable that irradiation of an oil drop with certain types of rays would result in oxidation of some of the molecules and as a consequence the drop would spread. Other chemical effects from irradiation indicate that one part in 20,000 can be changed with a large, but still reasonable dose.

For the first qualitative experiments, drops of petrolatum were placed on the surface of alkaline water in small shallow glass trays. Illumination was arranged so that light was reflected from the water surface and an image of the drop was projected, by means of a lens, to a vertically placed millimeter paper. One drop was irradiated with β-rays from a glass bulb containing about 90 mc of radon. Another drop was kept for control. The rays were filtered with about 0.2 mm brass and the bulb kept at about 1 cm distance from the drop. After one and a half hours the diameter of the drop had increased from 1.2 to 1.5 cm while the control drop had increased from 1.1 to 1.15 cm. After twelve hours of irradiation the diameters were 3.15 and 1.2 cm, respectively. The radon was removed and after twelve more hours the diameters were 3.25 and 1.2 cm. The second drop was then exposed for five and three quarters hours and the diameters afterwards measured 3.25 and 2.0 cm, respectively. This seemed to prove that the drops spread out over a larger surface as a consequence of exposure to rays from the radon. It seems reasonable to assume that the main effect is from the β-rays.

One drop of petrolatum on a water surface was next exposed to Röntgen rays. The container was placed inside the large drum containing the x-ray tube. The distance target to oil was 30 cm; the container was covered with black paper. Two hundred kilovolt peak and 30 ma were used and the drop was exposed for 64.5 minutes. The diameter increased 45 percent in size as compared to about 5 percent for the control drop. Evidently then Roentgen rays also have a spreading effect on oil drops on water.

Finally ultraviolet irradiation was tried. A quartz mercury lamp of the Cooper-Hewitt type

[1] Langmuir, Science **84**, 379 (1936); J. Chem. Phys. **1**, 756 (1933).

was used, running at 50 volts with about four amperes. The first drop was exposed for ten minutes at 12″ distance. It increased 80 percent in diameter and the control about 2 percent. A drop exposed under the same condition but with a piece of ordinary glass placed between the lamp and the container behaved like the control drop. When the exposure to ultraviolet radiation was extended for more than an hour the drop spread out to such a thin film that colored diffraction patterns could be seen.

From these preliminary experiments it is evident that β-rays, x-rays and ultraviolet rays, or radiation whose quanta are above a certain size, affect the oil drops in such a manner that they spread on water to an extent depending upon the amount of exposure. It seems reasonable to assume that a certain portion of the molecules are oxidized even though it would be difficult to determine the exact reaction.

It should be of interest to obtain some quantitative data and investigations of this nature have been started. The size of the drops have been measured by means of a telescope supplied with a scale arranged so that the diameter can be measured to within 0.1 mm. It is our intention to use some homogeneous hydrocarbons but the experiments reported here have been carried out with a mixture of long chain hydrocarbons in a heavy mineral oil referred to as Bacol which was easily obtainable.

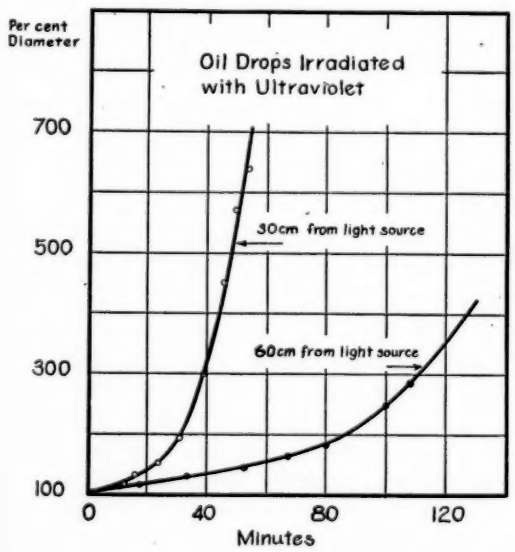

FIG. 1. Oil drops, on 0.01 *N* NaOH, irradiated with ultraviolet. Initial diameter of the drops was 5.3 mm.

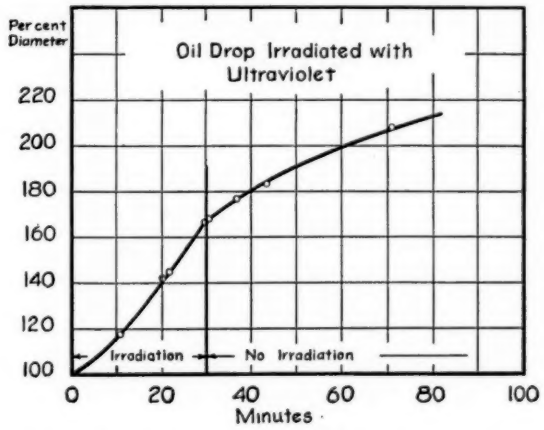

FIG. 2. An oil drop, on 0.01 *N* NaOH, irradiated for 30 minutes with ultraviolet at a distance of 30 cm from the lamp.

A number of factors may influence the spreading of the drop. The effect of impurities and of ions in the water is undoubtedly important. So far alkaline water consisting of 0.01 normal sodium hydroxide, made with distilled water, has been used for most experiments. No appreciable difference was, however, noticed in one experiment when 0.01 normal hydrochloric acid was used instead of sodium hydroxide. This was surprising as a drop of oil containing stearic acid behaved differently on acid water. The effect of temperature has not been determined as yet. The original size of the oil drop may be of considerable importance. Drops of nearly the same size and of an average weight of about 9 mg have been used for most experiments. The diameters of these drops were between $4\frac{1}{2}$ and 6 mm. For a few larger drops which were studied the percentage increase of the diameter during the time of irradiation with ultraviolet rays was smaller. If a large oil lens (consisting of about 25 drops) is given considerable radiation so that it becomes thin enough to show interference fringes and is left over night, the oil film becomes slightly thicker and a "solid" very thin and invisible film will cover the whole water surface. A small lens (one drop) behaves in a similar way but the film covering the water seems to have a "liquid" consistency. Mechanical agitation hastens the process. Apparently the attractive forces between the hydrophilic molecules and the oil molecules

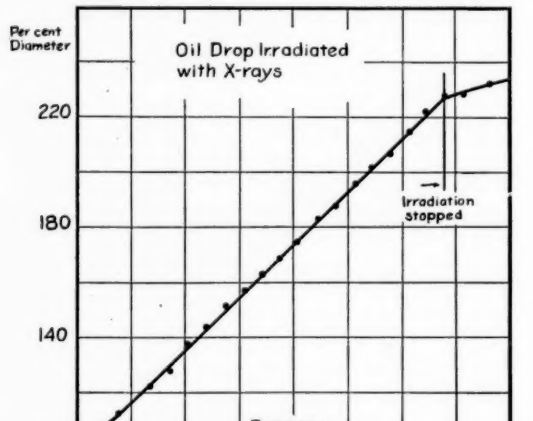

FIG. 3. An oil drop, on 0.01 *N* NaOH, irradiated with x-rays at 100 KVP, 5 ma, 20 cm distance from the target. Irradiation was stopped after 271 minutes.

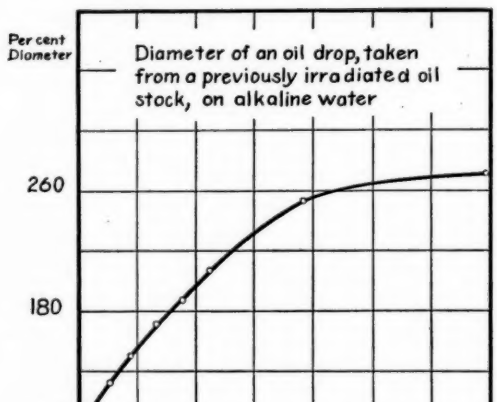

FIG. 4. Oil, completely filling a 25 cc glass-stoppered flask, was irradiated with x-rays at 200 KVP, 30 ma, 30 cm distance from target, for 232 minutes. Eighteen hours after the exposure a drop of this oil was placed on a 0.01 *N* NaOH and the relation between its diameter as a function of time was determined.

are not as great as those between the oil molecules.

For most of these experiments large watch glasses were used and the alkaline water had a surface measuring about 11 cm in diameter. A change in this diameter did not affect the spreading appreciably as long as the final diameter of the drop was less than half the diameter of the water surface.

The drops keep on spreading for a considerable length of time after the irradiation is discontinued. This is evidently due to a gradual diffusion of the changed molecules to the oil-water interface.

Fig. 1 shows the growth of two drops that were exposed to ultraviolet radiation. The growth is expressed in percent of the original diameter. Drop I was exposed at 30 cm distance and drop II at 60 cm distance from the lamp.

While it is impossible, from the curves, to say how closely the velocity of spreading is proportional to the intensity of radiation, because of the diffuse source of light, still there appears to be an approximate proportionality. The velocity of spreading of the drop at 60 cm distance compared to that at 30 cm distance, is probably greater than that expected from the ratio of the intensities, due to the greater proportion of chemically changed molecules having had time to diffuse to the water surface. To find the effect of a given quantity of radiation it will be necessary to compare the final diameters of the drops.

Fig. 2 shows the growth of a drop during and after the irradiation with ultraviolet light. The drop was at 30 cm distance from the lamp. Fig. 3 shows the growth of a drop during and after irradiation with x-rays. The diameter of the drop immediately before the irradiation was 7.2 mm; 100 KVP, 5 ma, 20 cm target skin distance, and no filter except a piece of black paper, was used. The half-value layer was 0.8 mm aluminum, and the intensity amounted to 240 roentgens per minute as measured in air. The container was placed on paraffin blocks and a large field was used. A drop exposed to β-rays from a radon bulb grew in a similar manner. These results give an idea of the velocity of the growth of the drops when they are exposed directly on the water surface. It is possible that this method could be used for measurements of intensity of radiation. The number of roentgens required for an appreciable growth of a drop is, however, so large that the method would be impractical for the measurements of x-rays. It may prove satisfactory for measurements of short wave ultraviolet radiation. It may also be tried to compare the surface effects of different types of rays, as the maximum thickness of the drops does not exceed 4 mm.

The effect of the radiation may take place

throughout the oil, at the whole surface of the drop, or at one of the interfaces. The fact that the drop grows after the irradiation is discontinued, indicates that the oil-water interface is not the sole place for immediate action. It may be considered possible that activated water molecules contribute to the reaction, but that could hardly explain the delayed effect. More information could evidently be obtained by irradiating the oil before the drop was placed on the water. In the first experiment of this type oil was kept in the same type of containers as used before, namely large watch glasses. A large surface thus was exposed to air. After the irradiation a drop of the oil was placed on a water surface. Such a drop has at first about the same diameter as a drop from unirradiated oil. It spreads, however, rather rapidly and reaches a limiting size after several hours. The final size depends upon the amount of radiation given. It might be expected that the amount of oil surface exposed to the air during irradiation would make a large difference in the chemical change. However, Fig. 4 shows that with oil completely filling a closed container during irradiation with x-rays, this change took place. This does not exclude air from the reaction, as amounts absorbed on the container walls and in the oil may be sufficient for the reaction.

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Reactions in the System Containing Nitrogen Dioxide, Carbon Monoxide and Oxygen; NO_3 as an Intermediate in the Classical Trimolecular Oxidation of Nitric Oxide

G. M. CALHOUN AND R. H. CRIST
Department of Chemistry, Columbia University, New York City

The kinetics of some reactions in the system containing carbon monoxide, oxygen, and nitrogen dioxide have been studied over the temperature range from 658° to 800°K. It has been shown that the reaction is heterogeneous for the lower pressures of nitrogen dioxide and homogeneous for pressures above 10 mm. The homogeneous portion of the reaction appears to include the oxidation of nitric oxide and the oxidation of carbon monoxide by "oxides" of nitrogen. A bimolecular reaction involving nitric oxide and oxygen has been studied. Evidence is presented which indicates that the oxidation of nitric oxide involves two consecutive bimolecular reactions instead of the classical termolecular mechanism.

INTRODUCTION

THE effect of small amounts of nitrogen dioxide upon certain thermal oxidation reactions has been described by several investigators. The rate of the oxidation of hydrogen catalyzed by traces of nitrogen dioxide has been studied by Hinshelwood and co-workers.[1] Norrish[2] has shown that a photochemical reaction proceeds in hydrogen-oxygen mixtures containing nitrogen dioxide at temperatures which are far too low to permit a measurable thermal reaction.

Mixtures of carbon monoxide and oxygen exhibit definite explosion areas which are sharply defined by temperature and pressure of the gases. Semenoff[3] found that these explosive peninsulas could be extended a hundred degrees or more in the direction of lower temperatures if a small quantity of nitrogen dioxide was added to the mixture. This work was primarily concerned with the study of the effect of various inert gases, water vapor, etc. upon the explosion limits. No data relative to the rate of the nonexplosive catalyzed reaction were reported.

A study of the nitrogen dioxide catalyzed oxidation of carbon monoxide in the nonexplosive region has been made by Crist and Roehling.[4] They indicated that the catalytic effect of nitrogen dioxide was probably due to

[1] (a) Gibson and Hinshelwood, Trans. Faraday Soc. **24**, 559 (1928); (b) Thompson and Hinshelwood, Proc. Roy. Soc. **124A**, 219 (1929).
[2] Norrish and Griffiths, Proc. Roy. Soc. **139A**, 147 (1933).
[3] Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935).
[4] Crist and Roehling, J. Am. Chem. Soc. **57**, 2196 (1935).

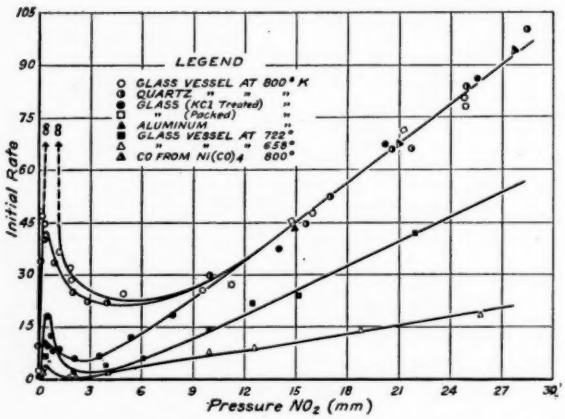

FIG. 1. The effect of surface on the catalyzed oxidation of carbon monoxide.

two processes, one of which was observed at low concentrations of the dioxide, while the other became important when the amount of the catalyst exceeded a certain value.

A preliminary investigation[5] has shown the catalyzed oxidation of carbon monoxide to be heterogeneous for small concentrations of nitrogen dioxide and essentially homogeneous for pressures of the catalyst above 10 mm. The first problem in the present work has been concerned with the measurement of the rate as a function of the surface and temperature over a wide range of catalyst concentration. Since the velocity of the heterogeneous reaction was greatly decreased in a vessel coated with potassium chloride, a separation of the two processes seemed likely, so that a study of the homogeneous catalysis was instituted. Rate measurements under different experimental conditions indicated two bimolecular reactions might be studied. It is with the determination of the rate constants and the temperature coefficients of these reactions that the major portion of this paper is concerned.

EXPERIMENTAL

The apparatus used in this investigation has been described.[4] The reaction vessel was placed in the well of a sulfur thermostat which was equipped with a barostat controlled by a vacuum tube relay.[6, 7] This device maintained the temperature constant to within ±0.3°C. Carbon monoxide and oxygen pressures were measured with mercury manometers and the nitrogen dioxide was measured by a Pirani-Hale type gauge. The progress of the reaction was followed by observing the decrease in pressure as denoted by a capillary mercury manometer.

Oxygen was admitted to the reaction vessel to the desired pressure, then the manometer was filled with oxygen or carbon monoxide to prevent nitrogen dioxide from coming in contact with the mercury surface during a run. Nitrogen dioxide was measured in the Pirani gauge, frozen into small U tube by means of liquid air, allowed to warm up and expand into the reaction vessel, and finally the last traces of the dioxide were carried into the reaction vessel by the carbon monoxide.

Carbon monoxide and nitrogen dioxide were prepared and purified by the methods described in a previous paper.[4] Nickel carbonyl was used as an independent source of carbon monoxide. The liquid carbonyl was taken from a commercial cylinder, fractionally distilled, then decomposed by passing the vapor through a furnace at 300–350°C. Great care was taken to remove traces of finely divided nickel and undecomposed nickel carbonyl. The purification train consisted of several liquid nitrogen traps and U tubes of activated charcoal cooled by liquid nitrogen. Oxygen was prepared by the electrolysis of a 15 percent potassium hydroxide solution using nickel electrodes. The gas was passed through a trap cooled by solid carbon dioxide into a furnace containing copper oxide at a dull red heat, then through a second dry-ice trap, and finally over phosphorous pentoxide.

RESULTS

The rate of oxidation of carbon monoxide in the presence of different quantities of nitrogen dioxide (0.1 to 30 mm) was observed for a variety of reaction vessels. The velocity of

TABLE I.

Standing Time for O_2 (min.)	0	1	5	10	15	45	100
ΔP (mm) 5→35 min.	48.0	45.8	41.8	36.4	34.8	28.8	26.0

[5] Crist and Calhoun, J. Chem. Phys. **4**, 696 (1936).
[6] Rittenberg and Urey, J. Am. Chem. Soc. **56**, 1885 (1934).
[7] Coffin, J. Am. Chem. Soc. **55**, 3646 (1933).

reaction for small nitrogen dioxide pressures is greatly affected by the surface, but with greater pressures the surface dependence is decreased, and finally disappears when the nitrogen dioxide exceeds 10 mm.

The heterogeneous reaction

In this study the carbon monoxide and oxygen were constant at 500 and 250 mm, respectively. A reaction vessel was selected and the relative rates were observed over the whole range of nitrogen dioxide pressures. In Fig. 1 the initial rate is shown as a function of nitrogen dioxide. The initial rates for the fast reactions were determined by drawing tangents to the rate curves at 1 min., and the relative rate was expressed for a ten minute interval. For the slow reactions, the pressure change from 5 to 15 min. was taken to represent the rates.

The reaction in glass at 800°K exhibits an explosive area between 0.3 and 1 mm of nitrogen dioxide. This region corresponds to the maximum rate in vessels which gave no explosions. The position of the maximum is practically the same as that found by Norrish[2] for the nitrogen dioxide sensitized hydrogen oxidation. The rate of the heterogeneous reaction was greatly decreased in a Pyrex vessel which had been treated with a potassium chloride solution. Results obtained in an aluminum vessel were very similar to those observed in quartz. Fig. 1 also includes runs in which carbon monoxide prepared from nickel carbonyl was used.

When quartz vessels were used, a slight modification in the experimental method was necessary, as it was found that the rate of the reaction depended on the length of time the oxygen was allowed to remain in contact with the quartz surface before introducing the other gases. A systematic study was made to determine this effect. The results are summarized in Table I. The rates in the second row are the pressure changes over a 30 minute time interval, and the other variable in this case is the standing time of oxygen in the quartz reaction vessel. The pressure of carbon monoxide and oxygen were constant at 500 and 250 mm, respectively, the nitrogen dioxide was 2.02 mm in all cases, and the temperature was 800°K. It can be seen that the effect is practically constant after 1 hr. and so, in rate measurements at low catalyst concentrations, the oxygen was always allowed to stand one hour before introducing the other gases. It must be pointed out that this phenomenon was *not* observed at *high* pressures of nitrogen dioxide, in fact the reaction in quartz at low pressures of the catalyst furnished the only example of this effect.

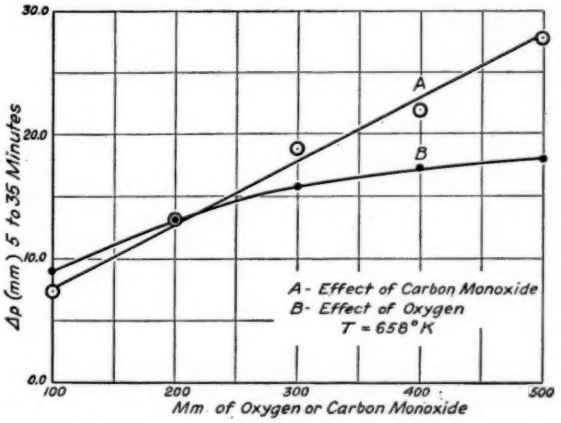

FIG. 2. The effect of carbon monoxide and oxygen on the homogeneous reaction.

The homogeneous reaction

A Pyrex reaction vessel, the surface of which was rinsed with a saturated solution of potassium chloride, was used in all measurements of the homogeneous reaction. In order to minimize any surface effect only the higher concentrations of the nitrogen dioxide were used.

A general study of the effect of the several components of the reacting system was made. The nitrogen dioxide was constant at 15.4 mm and the effect of the other gases was obtained by alternately keeping each constant while the other was varied. The results are shown in Fig. 2. The rate is expressed as the pressure change over a 30 min. time interval. This is a good measure of the rate because at this temperature (658°) the ration $\Delta P/\Delta t$ does not change appreciably during the interval selected. Fig. 2 shows that the rate is proportional to the first power of the carbon monoxide and to some lower power of the oxygen concentration.

Experiments with large excess of oxygen

Since no measurable homogeneous reaction between carbon monoxide and oxygen has been

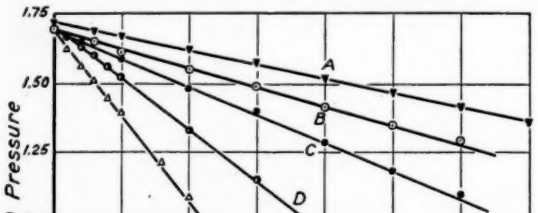

FIG. 3. Typical runs at high oxygen concentration: CO = 50 mm; O_2 = 600 mm; NO_2 = 1.52, 2.30, 3.22, 1.67, 2.42×10^{-7} mole cc^{-1} for *A*, *B*, *C*, *D* and *E*, respectively.

observed, it is quite likely that the formation of carbon dioxide in the gas phase is dependent on the nitrogen dioxide. Hence the results relative to the effect of oxygen shown in the preceding section would be expected on the basis of the equilibrium relation between nitrogen dioxide and oxygen, namely,

$$[NO_2]=A[O_2]^{\frac{1}{2}}/(K^{\frac{1}{2}}+[O_2]^{\frac{1}{2}});$$
$$A=[NO]+[NO_2],$$

as the observed rate was proportional to (NO_2) calculated from this equation over the range of oxygen pressure used. Further, with a large excess of oxygen the equilibrium concentration of nitrogen dioxide will probably be maintained. If also the carbon monoxide is quite low in concentration, the amount of oxygen lost during reaction will not be great enough to change the equilibrium concentration of nitrogen dioxide appreciably. The conditions for this series of experiments were: oxygen 600 mm, carbon monoxide 50 mm, and nitrogen dioxide 10 to 30 mm.

Representative experiments are shown in Fig. 3. Since the nitrogen dioxide is constant during any particular run, it is apparent that the rate is first order with respect to carbon monoxide. The constants calculated for curves *B* and *D* are given in Table II. Assuming that the reaction is principally between carbon monoxide and nitrogen dioxide with the latter constant and given by the equilibrium expression,[8] the constant, k_3, in the equation

$$-d(CO)/dt=k_3(CO)(NO_2)$$

may be calculated. The summarized results are given in Table III. Column 1 gives the experimental constant k'' which has already been defined, column 2 the equilibrium concentration of nitrogen dioxide, and the last column gives the bimolecular constant k_3 which is of course $k''/(NO_2)$.

The temperature dependence of k_3 can be expressed by the Arrhenius equation, namely,

$$k=A\exp(-E/RT).$$

Fig. 4 shows $\log k$ plotted against $1/T$. The constants in the preceding equation may be evaluated from the data to give

$$k_3=1.3\times10^{13}\exp(-32{,}200/RT).$$

The activation energy in this case is of the same order of magnitude as other homogeneous bimolecular reactions.[8]

Numerical errors in k_3 at 658° and 800° reported previously[5] have been corrected in Table III.

Experiments with low oxygen concentration

In preliminary experiments with the oxygen quite low, the slight temperature dependence

TABLE II. *Data for curves D and B of Fig. 3.*

763°K	$(NO_2)_{eq.}=1.67\times10^{-7}$ mole cc^{-1}	
t (min.)	Press. CO (mm)	$k''\times10^3$ $sec.^{-1}$
1	46.7	
2	43.1	1.30
3	39.9	1.30
4	36.3	1.39
5	33.5	1.38
10	21.5	1.43
15	14.3	1.40
25	5.9	1.44
		Av. = 1.38 ± .05
718°K	$(NO_2)_{eq.}=2.30\times10^{-7}$ mole cc^{-1}	
t (min.)	Press. CO (mm)	$k''\times10^4$ $sec.^{-1}$
1	48.5	
3	44.5	5.17
5	41.3	5.65
10	35.3	5.40
15	30.9	5.10
20	26.1	5.23
25	22.5	5.16
30	19.7	5.02
35	17.3	4.95
40	14.5	5.05
		Av. = 5.24 ± .17

The constant k'' is defined by the first-order equation $-d(CO)/dt = k''(CO)$.

[8] Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, 1932).

suggested that a reaction, other than the bimolecular process already mentioned, was being measured. The experimental conditions for this study were: oxygen 20–25 mm, carbon monoxide 600 mm, and the nitric oxide 10–30 mm (measured as nitrogen dioxide but largely dissociated into nitric oxide and oxygen after introduction into the reaction vessel). The total oxygen present was obtained by adding to the original oxygen introduced that produced by the decomposition of nitrogen dioxide. These gases were allowed to come to equilibrium before introducing the carbon monoxide. At equilibrium the oxygen furnished by the dioxide may be obtained from the expression

$$(NO_2)=A(O_2)^{\frac{1}{2}}/(K^{\frac{1}{2}}+(O_2)^{\frac{1}{2}}),$$

where A is the original nitrogen dioxide and K is the equilibrium constant.

The effect of oxygen on the rate was found by the examination of individual runs where the pressure change is a direct measure of the oxygen lost. The results in Table IV represent typical runs and show that the rate is first order with respect to oxygen. These results indicate that the effect of nitric oxide is constant during an individual run. The effect of changing the original nitric oxide may be seen in Fig. 5 in which the first-order constants k' for the individual runs are plotted against the corresponding nitric oxide concentration for several temperatures, the data for each point being similar to that represented in Table IV.

TABLE III. *Summary of results for runs with high oxygen.*

658°K	Equil. conc. NO_2	
$k''\times10^5$ (sec.$^{-1}$)	mole/cc$\times10^7$	$k_3\times10^{-2}$ (cc mole^{-1} sec.$^{-1}$)
8.45	3.11	2.72
10.8	4.20	2.57
7.08	2.34	3.03
		Av.=2.76±.17
718°		
52.4	2.30	22.8
81.4	3.22	25.3
43.8	1.85	23.7
63.0	2.66	23.7
35.4	1.52	23.2
		Av.=23.8±.50
763°		
106	1.29	82.3
205	2.18	94.0
81.8	.956	85.5
138	1.67	83.0
244	2.66	91.9
224	2.42	92.5
		Av.=88.0±4.7
783°		
164	1.14	144
151	1.01	149
292	1.99	146
213	1.52	140
		Av.=145±3.0
800°		
262	1.20	218
274	1.20	228
120	.575	209
176	.860	205
310	1.42	218
		Av.=216±7.0

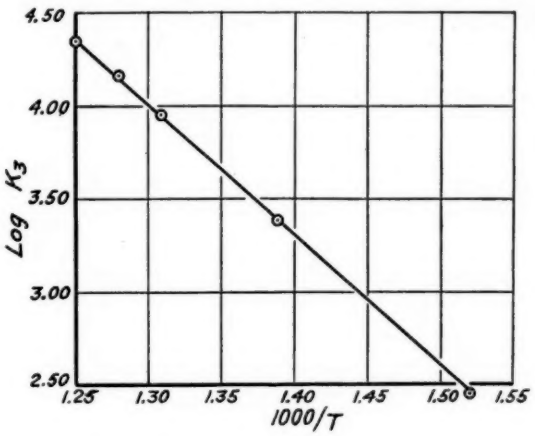

FIG. 4. Temperature dependence of k_3.

It is apparent that the effect is linear and can be expressed by

$$k'=k_1(NO).$$

Most of the runs indicated by Fig. 5 were with 600 mm of carbon monoxide. However, at 800° for (NO)=37, 33 and at 658° for (NO)=45, 29 the carbon monoxide was 250, 300, 235, and 300 mm, respectively. These points agree well with the values for the higher carbon monoxide pressures and show that the reaction is independent of this component. Therefore the rate equation expressing these results is

$$-d(O_2)/dt=k_1(NO)(O_2).$$

Table V gives the values of k_1 for the different temperatures as obtained from the slopes of the straight lines in Fig. 5.

The plot of $\log k_1$ against $1/T$ is shown in Fig. 6. The curvature can scarcely be attributed to experimental error and might then be considered as a variation of the activation energy with temperature.

TABLE IV. *Typical runs with low O_2.*

t (min.)	Press. O_2 (mm)	$k' \times 10^4$ (sec.$^{-1}$)
$T = 658°K$	(NO) $= 4.25 \times 10^{-7}$ mole cc^{-1}	
0	22.9	3.06
5	21.0	3.10
10	19.2	3.15
15	17.4	3.16
20	16.0	3.05
25	14.4	3.20
30	13.3	3.18
35	11.8	2.66*
40	10.8	3.08
60	7.6	Av. $= 3.12 \pm .05$
$T = 800°K$	(NO) $= 5.50 \times 10^{-7}$ mole cc^{-1}	
0	(25.0)	
5	20.3	6.90*
10	16.6	5.97
15	13.8	6.45
20	11.6	6.25
25	9.7	6.19
30	8.3	5.97
35	6.8	6.10
		Av. $= 6.16 \pm .14$

* Not included in average.

La Mer[9] has pointed out that there is no *a priori* reason for assuming the energy of activation to be independent of temperature. On integrating the Arrhenius equation, one ordinarily neglects the heat capacity of activation which, according to this author, has no more justification than the omission of the corresponding entropy terms in the calculation of a thermodynamic equilibrium. He suggests further, that since the temperature variation of activation energy is frequently within the limits of experimental error, it is usually detectable only in those measurements which carry high enough precision or in which the temperature interval can be made comparatively large. The activation energies obtained from the slopes of the curve in Fig. 6 are about 1000 and 5500 cal. for 680° and 780°, respectively. Assuming the foregoing interpretation to be applicable to the case at hand, the heat capacities of activation are calculated to be roughly 25 and 78 cal. per degree at 680° and 780°, respectively.

DISCUSSION OF RESULTS

The heterogeneous reaction

The explosive character of the heterogeneous reaction for proper conditions of surface and nitrogen dioxide concentration indicates that chains are initiated at the walls and extend out into the gas phase in sufficient numbers so as to produce explosion.[10] When the nitrogen dioxide pressure is below that required for an explosion, the rate is proportional to the concentration of the catalyst, so that the initiation or the propagation of the chains or both are directly dependent on this component. That the initial process involves a selective adsorption on the surface is shown by the data giving the effect of allowing the various gases to stand in contact with the surface before introducing the other reactants. No effect was observed for carbon monoxide and nitrogen dioxide, but there is a considerable retarding effect for oxygen in quartz vessels as shown in Table I. The individual runs in quartz could not be subjected to a thorough analysis, but they showed the rate to be quite uniform throughout, i.e., there was no high initial rate as in Pyrex where the rate was quite rapid for the first few minutes and then dropped off abnormally. The oxygen appears to exert a "buffer" action upon the surface of quartz in that it permits only a limited number of chains to be initiated per unit time; on the other hand, oxygen covers less of the glass surface, hence the high initial or explosive rate. The data could be explained on the assumption that chains originate

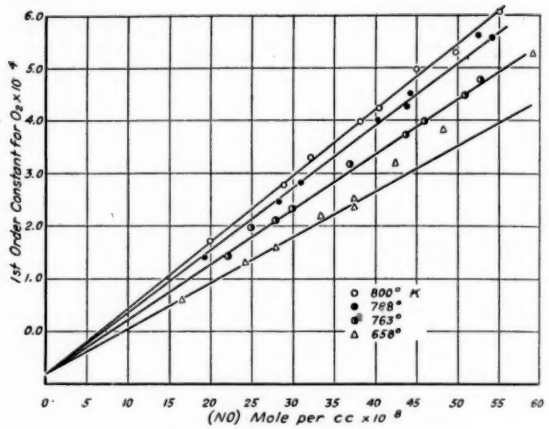

FIG. 5. The effect of nitric oxide at low oxygen concentrations.

TABLE V. k_1 (*cc mole*$^{-1}$ *sec.*$^{-1}$) $\times 10^{-3}$.

T°K	800	788	763	658
k_1	1.28	1.20	1.07	0.865

[9] La Mer, J. Chem. Phys. **1**, 289 (1933).

[10] Alyea, J. Am. Chem. Soc. **53**, 1324 (1931).

from nitric oxide or nitrogen dioxide adsorbed on the surface, and that the chain originator is displaced from the surface by oxygen molecules.

Norrish[2, 11] has pointed out that the close similarity in photochemical and thermal reactions in the system, hydrogen-oxygen-nitrogen dioxide suggests that chains may be initiated by oxygen atoms. Thus it is clear that in the photo process oxygen atoms may be produced by illumination

$$NO_2+h\nu \rightarrow NO+O$$

but a source of oxygen atoms in the thermal reactions is not quite so obvious. The following possibilities have been suggested

$$NO_2 \rightarrow NO+O-72.6 \text{ kcal.},$$
$$NO+O_2 \rightarrow NO_2+O-44 \text{ kcal.}$$

The chains might be propagated by ozone molecules as suggested by the work of Jackson.[12]

An empirical equation for the rate as a function of the pressure of nitrogen dioxide over the range of the heterogeneous reaction has been given by Crist and Roehling[4] and Norrish[11] namely,

$$y=ax/(x^2-bx+c),$$

where x is the nitrogen dioxide concentration and y is the rate. The shape of the curve can be accounted for if one assumes with Norrish that the rôle of nitrogen dioxide is threefold: (1) it originates chains by furnishing oxygen atoms, (2) it acts as an inhibitor breaking chains in the gas phase and on the walls, (3) as a branching factor.

The homogeneous reaction between carbon monoxide and nitrogen dioxide

In experiments for which the oxygen was quite high in concentration, it was assumed that the equilibrium amount of nitrogen dioxide was present during a run. It was also found that the rate depends on the oxygen as indicated in the nitric oxide-nitrogen dioxide equilibrium. The results obtained in the system with very low oxygen indicate that NO_3 is formed as an intermediate in the oxidation of nitric oxide. If such is the case, then there is the question as to whether the oxidation of carbon monoxide is by

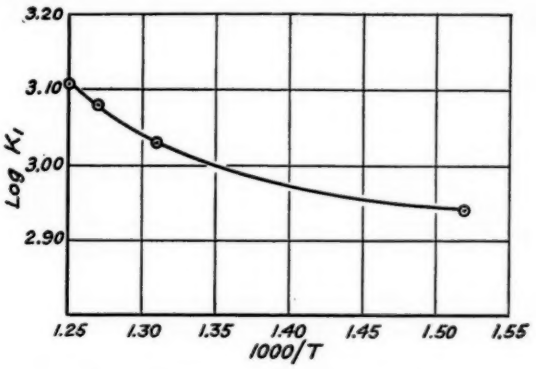

FIG. 6. Temperature dependence of k_1.

reaction with nitrogen dioxide, NO_3, or both. A bimolecular constant for the oxidation of carbon monoxide was calculated using the nitrogen dioxide concentration given by the equilibrium expression. Of course, if a large portion of the reaction occurs by way of NO_3, the numerical value of k_3 will be in doubt. The relationship of the rate with respect to oxygen suggests that the principal reaction under these conditions is that by way of nitrogen dioxide.

An alternative explanation may be advanced if one assumes that carbon monoxide reacts with NO_3 but not NO_2. If such is the case, the observed temperature dependence of k_3 (Table V) might be explained as being essentially due to the rapid decrease in the nitrogen dioxide concentration with temperature. Thus, as the concentration of nitric oxide increases and likewise the amount of NO_3, the rate increases. If the reaction of carbon monoxide and NO_3 is rate determining and has a small temperature coefficient, then the results in question might be accounted for on the basis of the temperature coefficient for the bimolecular decomposition of nitrogen dioxide (E_{ACT} about 30 kcal.). On the basis of the present data one cannot decide definitely which of the above interpretations is correct, but we are inclined to favor the first explanation.

Nitrogen oxide oxidation (low oxygen expt's.)

In a preliminary communication[5] we assumed that the oxidation of nitric oxide was a trimolecular process. Accordingly, a third-order rate constant involving the square of the nitric oxide and the first power of the oxygen con-

[11] Foord and Norrish, Proc. Roy. Soc. **152A**, 196 (1935).
[12] Jackson, J. Am. Chem. Soc. **56**, 2631 (1934).

centration was calculated. It was suggested that the decrease in our constant at high nitric oxide concentration might be due to the reverse reaction. Subsequent data and a comparison of the relative rate of the reaction of the carbon monoxide with nitrogen dioxide and the bimolecular decomposition of nitrogen dioxide, have shown that the latter reaction could not account for the large discrepancy in the third-order constant.

Let us assume for the present that the following reactions comprise the homogeneous portion of the reaction

$$2NO+O_2\rightarrow 2NO_2, \quad (1)$$

$$2NO_2\rightarrow 2NO+O_2, \quad (2)$$

$$NO_2+CO\rightarrow CO_2+NO. \quad (3)$$

With small amounts of oxygen it was found that the rate was first order with respect to oxygen and nitric oxide and independent of the carbon monoxide. This would eliminate (3) as the rate determining step. It is evident that if the concentration of nitrogen dioxide is too small to influence the rate through (3) it would be much too small for (2) to be important. Hence (1) is left as the rate determining step and this requires the square of the nitric oxide rather than the first power as found in the experiments. Consider then the following reactions:

$$NO+O_2\rightarrow NO_3, \quad (4)$$

$$NO_3+CO\rightarrow NO_2+CO_2, \quad (5)$$

$$NO_2+CO\rightarrow NO+CO_2, \quad (3)$$

$$NO_3+NO\rightarrow 2NO_2, \quad (6)$$

$$2NO_2\rightarrow 2NO+O_2. \quad (2)$$

Nos. (3) and (5) are eliminated because the rate does not depend on carbon monoxide. (6) would show a tendency to change to second order with respect to nitric oxide which was not observed within the precision of the data except at the lowest temperature. This leaves (4) as the rate determining reaction.

It must be added that at the lowest temperature, reactions (2) and/or (6) are probably important, for the points (Fig. 5) deviate considerably from the straight line at high nitric oxide values. The uncertainty in the initial oxygen pressure might account for this deviation. In all these measurements the *total* oxygen was about 20–25 mm; the oxygen furnished by the decomposition of nitrogen dioxide was about $0.6\,A/2$ because the equilibrium concentration of the latter at 658°K for 20–25 mm oxygen is approximately 0.4 A, where A is the original nitrogen dioxide. For relatively small A values, the amount of oxygen furnished by the nitrogen dioxide is a smaller fraction of the total oxygen than the quantity contributed by the dioxide when the A value is large since in all cases the total oxygen was 20–25 mm. By comparison of the rates of disappearance of nitrogen dioxide by way of bimolecular decomposition and by reaction with carbon monoxide, it can be shown that the amount of dioxide lost by the former process is appreciable when A is large. This means that more oxygen is being furnished to the reaction mixture during the run, which of course affects the estimate of the original oxygen concentration.

A calculation for two A values gives an indication of the error in the estimation of the initial oxygen concentration. Using $A=3\times10^{-7}$ (equilibrium concentration) the loss of nitrogen dioxide per second by reactions (2) and (3) would be

$$-d(NO_2)/dt=k_3(NO_2)(CO)$$
$$=2.70\times10^2\times3\times10^{-7}\times1.46\times10^{-5}=11.9\times10^{-10}, \quad (3)$$

$$-d(NO_2)/dt=k_2(NO_2)^2$$
$$=5\times10^3\times9\times10^{-14}=4.5\times10^{-10}. \quad (2)$$

Thus (2) represents 27 percent of the total loss of nitrogen dioxide in this case and a similar calculation using $A=1\times10^{-7}$ shows that (2) would account for only 11 percent of the total. From the consideration of the several rate equations it is possible to estimate the rate of change in nitrogen dioxide concentration with time. Then calculation shows that the estimates for the original oxygen concentration may be too small by approximately 10 percent in the case of the high nitric oxide values at 658°K. The points at the higher temperature are not likely to be much in error due to these competing reactions because the value of nitrogen dioxide at equilibrium is only $0.1A$ as compared to $0.4A$ at the lowest temperature.

Concluding Remarks

The rate of the nitric oxide oxidation has been measured by Bodenstein,[13] Briner, Pfeiffer and Malet,[14] and others. The third-order constants obtained by these investigators do not distinguish between a trimolecular process and two consecutive bimolecular reactions. Kassel[8] has estimated the number of trimolecular collisions in an imperfect gas and the results of his calculation show that the collision number is certainly large enough to account for the observed rate. Gershinowitz and Eyring[15] have obtained a theoretical expression for the rate of trimolecular reactions which involves a ratio of partition functions for the "activated" complex and the normal reactant molecules. Their calculated values for the oxidation of nitric oxide agree well with experiment. This theoretical treatment, like previous experimental work, cannot distinguish possible intermediate reactions which may lead finally to the formation of the activated state.

Recently, Rice[16] has suggested that the oxidation may occur in two steps

$$2NO \rightleftarrows (NO)_2, \qquad (1)$$

$$(NO)_2 + O_2 \rightarrow 2NO_2. \qquad (2)$$

If the equilibrium in (1) is maintained, the rate should be determined by (2) and the observed order of the reaction would be unchanged. The abnormal entropy of vaporization of liquid nitric oxide is taken as evidence for the existence of $(NO)_2$ in the gaseous phase. He estimates the heat of dissociation in the gas phase to be 2–3000 cal. and this could account for the negative temperature coefficient of (2) since the concentration of the associated complex should decrease with temperature. Trautz[17] suggested some years ago that the oxidation of nitric oxide might include the formation of a complex, NO_3, as an intermediate.

$$NO + O_2 \rightleftarrows NO_3, \qquad (1a)$$

$$NO_3 + NO \rightarrow 2NO_2. \qquad (2a)$$

This author's justification for the intermediate complex included the idea that the number of three-body collisions could not account for the observed rate. The data given in the present paper requires this intermediate on the grounds that the observed rate is dependent on the first power of the nitric oxide concentration. It is only necessary to postulate that the NO_3 is removed rapidly by the carbon monoxide, thus preventing its dissociation or reaction with nitric oxide.

The temperature coefficient of (1a) indicates a small positive activation energy, hence the rate of formation of NO_3 will not increase greatly with temperature, but the unimolecular decomposition of this complex might have a somewhat greater temperature dependence. If this is true, the concentration of the NO_3 will decrease with temperature and reaction (2a) should show a negative temperature coefficient. In the absence of carbon monoxide, the equilibrium in (1a) will be maintained and the rate determining reaction would be (2a) which involves the second power of the nitric oxide concentration. Thus, one can correlate the present work with that of Bodenstein and others.

[13] Bodenstein, Zeits. f. Elektrochem. **24**, 183 (1918).
[14] Briner, Pfeiffer and Malet, J. Chem. Phys. **21**, 25 (1924).
[15] Gershinowitz and Eyring, J. Am. Chem. Soc. **57**, 985 (1935).
[16] O. K. Rice, J. Chem. Phys. **4**, 53 (1936).
[17] Trautz, Zeits. f. Elektrochem. **22**, 104 (1916).

Bimolecular Association Reactions.*

GEORGE E. KIMBALL
Department of Chemistry, Columbia University, New York, N. Y.

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By means of classical vibration theory a method is developed for estimating the mean lifetimes of the unstable molecules formed by the reaction of two polyatomic radicals. It is shown that these lifetimes are usually long in comparison with the time between collisions, except for the very simplest radicals. Approximate lifetimes for a number of these unstable molecules are given. From these values the orders of the corresponding association reactions may be predicted.

INTRODUCTION

BIMOLECULAR association reactions play an important rôle in the kinetics of homogeneous gas reactions, especially in chain reactions, the whole kinetics of which often depend on whether a chain breaking association reaction is of the second or third order. Direct experimental evidence of the order of these reactions is difficult to obtain, and is usually complicated by side reactions.

The explanation of why these reactions are sometimes second order and sometimes third order was originated by Herzfeld[1] and developed by a number of others.[2] It is now generally accepted that a molecule formed by the association of two radicals can only exceptionally lose its energy of formation as radiation, or convert any appreciable part of it into rotational energy or energy of electronic excitation. All the energy of formation is therefore present as vibrational energy, and unless the molecule is deactivated by collision with another molecule it will eventually redissociate. If the "mean life" of the new molecule is long compared with the mean time between collisions (about 10^{-11} sec.) the reaction is of the second order, while if the "mean life" is short, the reaction is of the third order.

Rosen[3] has computed the mean life of a linear triatomic molecule by quantum-mechanical methods. His method, however, is so complicated that it is very difficult to apply. It therefore seems better to give up the use of quantum mechanics and treat the problem classically. The results will, of course, be only approximate, but even a knowledge of the orders of magnitude of the mean lives of these molecules is of great value.

GENERAL THEORY

In order to specify the positions of the atoms of the new molecule we shall use a set of coordinates $x_0, x_1, \cdots x_n$, of which x_0 is the displacement from equilibrium of the bond just formed, and the remaining coordinates are the displacements of the other bonds and bond angles. Now for the theory of small vibrations of the molecule certain "normal" coordinates are introduced. These may be defined in terms of the x_i by a set of equations

$$\xi_i = \sum_j a_{ij} x_j \quad (i=0, 1, \cdots n), \tag{1}$$

which may be solved for the x_i:

$$x_i = \sum_j b_{ij} \xi_j \quad (i=0, 1, \cdots n). \tag{2}$$

The motion of the system is then represented at any time when all the x_i are small by

$$\xi_i = \xi_i^0 \cos \vartheta_i \tag{3}$$

or

$$x_i = \sum_j b_{ij} \xi_j^0 \cos \vartheta_j, \tag{4}$$

where the ξ_i^0 are constants determined by the initial conditions and ϑ_i is of the form

$$\vartheta_i = 2\pi \nu_i t + \epsilon_i, \tag{5}$$

where ν_i is the frequency and ϵ_i is the initial phase of the ith mode of vibration.

Eqs. (3), (4) and (5) describe the motion of the molecule only insofar as the forces acting are harmonic, i.e., as long as the x_i are so small that

* Presented at the Pittsburgh Meeting of the American Chemical Society, September, 1936.

[1] Herzfeld, Zeits f. Physik **8**, 132 (1922).

[2] Cf. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932), Chapter III.

[3] Rosen, J. Chem. Phys. **1**, 319 (1933).

the potential energy can be expressed in the form $V=\sum_i \frac{1}{2}k_i x_i^2$. In Fig. 1 is shown the actual form of the potential energy of one of the bonds. Instead of following the parabola $V=\frac{1}{2}kx^2$ (shown as a dotted line) the potential energy approaches the limiting value D as x becomes large. After the point M is reached the restoring force decreases instead of increasing, and consequently the acceleration produced is smaller.

If we compare the motions of two systems, one with the harmonic potential $OMA'B'C'$ and one with the potential $OMABC$, we find that there are many corresponding features. If, for example, the two systems are started at O with the same velocity, and the first system reaches its maximum displacement at A', the maximum displacement of the second system is at the corresponding point A. Upon returning to O the systems will again be moving with the same velocity, but on the other hand the times taken for the two vibrations will not be the same, that of the vibration from O to A' to O being shorter than that from O to A to O.

In describing the actual motion it is therefore convenient to introduce a new set of variables $\bar{x}_i$, which are related to the x_i by the equation

$$\frac{1}{2}k\bar{x}^2=V(x),$$

i.e., in such a way that the $\bar{x}$ of the point A is the x of the corresponding point A'. As long as the displacements are small, the x's and the $\bar{x}$'s are the same. In the same way we may introduce a set of variables $\bar{\xi}_i$ which are the same functions of the $\bar{x}_i$ as the ξ_i are of the x_i.

If we consider a single vibration in terms of its $\bar{x}$ we find that the motion may be expressed again by the equation $\bar{x}=\bar{x}^0\cos\vartheta_i$, i.e., the motion still lies between the limits $\bar{x}=\bar{x}^0$ and $\bar{x}=-\bar{x}^0$,

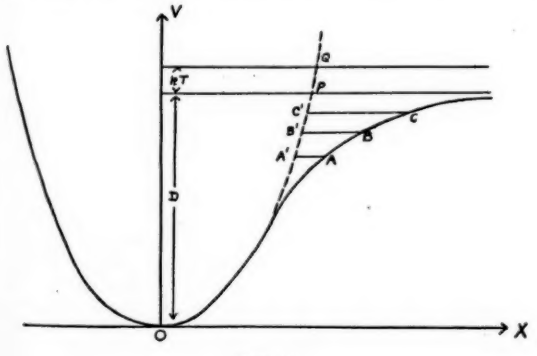

FIG. 1.

but because of the anharmonicity of the potential the angle ϑ no longer increases linearly with the time, but instead with a more complicated function of the time. The same conclusion holds true (at least to a first approximation[4]) in the coupled vibrations of molecules: Eqs. (3) and (4) still are good if we replace the x's and ξ's by the $\bar{x}$'s and $\bar{\xi}$'s, but Eq. (5) is no longer valid.

The values of the $\bar{\xi}_i^0$ must be calculated from the initial conditions. We assume that initially the molecule is at rest except for a motion of the coordinate x_0, which we assume to be decreasing in such a way that the energy of relative motion of the two colliding radicals is kT. In terms of the $\bar{x}_0$ this is equivalent to the motion of a harmonic system started at rest ($\dot{\bar{x}}_i=0$) and with all the $\bar{x}_i=0$ except $\bar{x}_0$, to which we give such a value that the total energy is $D+kT$. In terms of Fig. 1 this corresponds to a motion from rest at the point Q, or $\bar{x}_0=[2(D+kT)/k_0]^{\frac{1}{2}}$.

The condition $\dot{\bar{x}}_i=0$ requires that $d(\cos\vartheta_i)/dt=0$, i.e. that $\vartheta_i=0$, $\cos\vartheta_i=1$, and $\bar{\xi}_i=\bar{\xi}_i^0$. Putting the given values of the $\bar{x}_i$ into (1) then gives

$$\bar{\xi}_i^0=a_{i0}[2(D+kT)/k_0]^{\frac{1}{2}}. \tag{6}$$

The motion of the new bond is then found by putting this into (4) (with $i=0$)

$$\bar{x}_0=[2(D+kT)/k_0]^{\frac{1}{2}}\sum_j a_{j0}b_{0j}\cos\vartheta_j. \tag{7}$$

Dissociation will take place when $\bar{x}_0$ becomes greater than $(2D/k_0)^{\frac{1}{2}}$, that is, when the potential energy of the bond becomes greater than D. The condition for this is

$$\sum_j a_{j0}b_{0j}\cos\vartheta_j>[D/(D+kT)]^{\frac{1}{2}}. \tag{8}$$

Since kT is usually small compared to D this may be put into the simpler form

$$\sum_j a_{j0}b_{0j}\cos\vartheta_j>1-kT/2D. \tag{9}$$

Among the terms on the left of this equation some will vanish because the product $a_{j0}b_{0j}$ vanishes. The values of the corresponding ϑ_j are immaterial. Since $\sum a_{j0}b_{0j}=1$ and $kT/2D$ is usually small, the remaining cosines must have values near unity for (9) to be satisfied, i.e., the values of the ϑ_i must be near 0 after subtraction of an appropriate multiple of 2π. If there remain

[4] The basis for this statement is a series of numerical integrations of equations of motion of simple molecules.

$q+1$ terms in (9) after discarding those which vanish, and if we expand the remaining cosines, retaining only the first two terms of the expansion, Eq. (9) reduces to

$$\vartheta_0^2/r_0^2+\vartheta_1^2/r_1^2+\cdots+\vartheta_q^2/r_q^2<1, \quad (10)$$

where we have put

$$r_j^2=kT/a_{j0}b_{0j}D. \quad (11)$$

The physical significance of Eq. (10) is simply that dissociation will take place only if all of the modes of vibration are in phase at a time when the normal coordinate ξ_0 is at its maximum value, or nearly so. No great error will be introduced if we assume instead that Eq. (10) must be satisfied when this coordinate is exactly at its maximum value, i.e., when $\vartheta_0=0$. At this instant the condition (10) is

$$\vartheta_1^2/r_1^2+\vartheta_2^2/r_2^2+\cdots+\vartheta_q^2/r_q^2<1. \quad (12)$$

Since we know nothing of the values which the remaining ϑ_j have at such an instant, the only possible thing to do is to assume that all values of the ϑ_j are equally probable. The probability that Eq. (12) is satisfied is then the ratio of the volume of the q-dimensional ellipsoid determined by (12) to the volume $(2\pi)^q$ of the q-dimensional cube of allowed values for the ϑ_j. This ratio is given by[5]

$$r_1r_2\cdots r_q/2^q\pi^{q/2}\Gamma(q+2/2). \quad (13)$$

The probable number, N, of vibrations before dissociation is the reciprocal of (13), which becomes, on substituting for the r's and putting $a_{j0}b_{0j}=c_j^2$,

$$N=2^q\pi^{q/2}\Gamma(q+2/2)(D/kT)^{q/2}c_1c_2\cdots c_q. \quad (14)$$

The mean life is then obtained by dividing this expression by the frequency, ν_0, with which ϑ_0 vanishes:

$$\tau=N/\nu_0. \quad (15)$$

Determination of the c_i

Before Eq. (14) can be applied the quantities c_i must be determined. In view of the number of approximations which have already been made, the labor of the usual procedure for finding the normal coordinates of the molecule is hardly justified. A set of empirical rules has therefore been developed which gives estimates of the c_i which are as reliable as necessary for these purposes when the normal coordinates are not known exactly.

In a large number of molecules the number of possible interactions with the new bond is limited by the symmetry of the molecule. For example, if the molecule is linear, there is no tendency for the "bending" vibrations to couple with the vibrations along the axis. The two types of vibration are therefore completely distinct, and only the longitudinal vibrations need be considered.[6]

The best method of using the symmetry properties of the molecule is to introduce first a set of "symmetry coordinates."[7] These symmetry coordinates are formed by taking linear combinations of the coordinates x_i corresponding to each type of vibration in such a way that the new coordinates form irreducible representations of the symmetry group of the molecule. Thus, for example, if the molecule being formed is CH_3Cl (symmetry C_{3v}), we combine the three C−H stretching coordinates into three new coordinates, one of which belongs to the representation A_1, and two of which belong to the representation E. The C−Cl stretching coordinate is already a symmetry coordinate belonging to A_1, and the five "bending" coordinates form one symmetry coordinate belonging to A_1, and four belonging to E.

The c_i^2 we wish to determine are essentially the fractions of the normal coordinates which make up the bond being formed. By expressing the new bond in terms of these symmetry coordinates it is easy to find what fraction of the bond belongs to each representation of the group of the molecule. It only remains to divide these fractions among the various normal coordi-

[5] This expression cannot be used when any of the r's are greater than π, for then the ellipsoid projects beyond the cube. In such a case the expression for the probability would be much more complicated, but fortunately no such case has arisen in this work.

[6] This does not imply that there will be no bending of the newly formed molecule, for the motion of the molecules at the moment of collision will have components perpendicular to the axis. This motion, however, will have only the ordinary thermal energy, and in any case has no appreciable effect on the longitudinal vibrations.

[7] For a complete account of the group-theoretical methods used here, cf. Rosenthal and Murphy, Rev. Mod. Phys. **8**, 317 (1936).

TABLE I.

REACTION	q	N	τ(sec.)
$H+CN \rightarrow HCN$	1	11	1.2×10^{-13}
$Cl+CN \rightarrow ClCN$	1	8	4.7×10^{-13}
$Br+CN \rightarrow BrCN$	1	6	4.5×10^{-13}
$I+CN \rightarrow ICN$	1	5	4.0×10^{-13}
$O+CO \rightarrow CO_2$	1	40	6.2×10^{-13}
$CN+CN \rightarrow (CN)_2$	1	8	1.1×10^{-13}
$H+OH \rightarrow H_2O$	2	290	2.7×10^{-12}
$H+O_2 \rightarrow HO_2$	2	120	1.1×10^{-12}
$H+CH_3 \rightarrow CH_4$	2	290	3.2×10^{-12}
$Cl+CH_3 \rightarrow CH_3Cl$	2	73	4.4×10^{-12}
$Br+CH_3 \rightarrow CH_3Br$	2	61	4.3×10^{-12}
$I+CH_3 \rightarrow CH_3I$	2	45	3.6×10^{-12}
$CH_3+CH_3 \rightarrow C_2H_6$	2	73	2.4×10^{-12}
$OH+OH \rightarrow H_2O_2$	4	9×10^3	3×10^{-10}
$CH_3+OH \rightarrow CH_3OH$	4	2×10^4	5.6×10^{-10}
$H+CH_2Cl \rightarrow CH_3Cl$	5	1×10^6	1.2×10^{-8}
$NO_2+NO_2 \rightarrow N_2O_4$	10	8×10^7	5×10^{-6}
$H+C_2H_5 \rightarrow C_2H_6$	12	2×10^{14}	2.1
$Cl+C_2H_5 \rightarrow C_2H_5Cl$	12	1×10^{14}	6.3

nates belonging to the representations. To do this a simple empirical rule has been observed. Of the fraction of the bond belonging to any representation, each normal coordinate except the one arising principally from the symmetry coordinate in terms of which the new bond was first expressed takes 5 percent, the remainder belonging to the normal coordinate just mentioned. This rule has no theoretical justification, but gives in most cases an approximation good enough for the purposes of this paper.

For example, if we consider the reaction $H+CH_2Cl$ the bond x_0 is one of the C−H stretching coordinates, which, in terms of the symmetry coordinates already mentioned, is the sum of one coordinate belonging to A_1 and one belonging to E. We therefore assign one-half of the bond to each representation. In A_1 there are two other symmetry coordinates (the C−Cl stretching and a C−H bending) so we assign 5 percent of 0.5 or 0.025 to each, leaving 0.4 for the C−H stretching coordinate of this representation. In E we may have interaction with two types of C−H bendings, so we assign 5 percent of 0.5 or 0.025 to each of these, again leaving 0.4 to the C−H stretching. We have, therefore, the following set of c_i^2:

$$c_0^2=0.4,\quad c_1^2=0.025,\quad c_2^2=0.025,$$
$$c_3^2=0.4,\quad c_4^2=0.025,\quad c_5^2=0.025.$$

This approximate method of finding the c_i is very rapid in practice, and in all the cases in which it has been checked against actual calculations of normal coordinates has proved to give fair agreement.

RESULTS

In Table I are shown the results of a number of calculations made by this method. In this table are given q, the number of vibrations interacting with the new bond, N, the number of vibrations before dissociation, and τ, the mean life of the molecule formed. These calculations have been made for a temperature of 300°K. From Eq. (14) it is seen that the mean life varies as the $-q/2$ power of T, so that the mean life for any other temperature can be obtained by multiplication of these values by $(300/T)^{q/2}$.

In many cases other reactions are possible than the simple association considered here. While these possibilities have not been considered in detail, it is evident that if the life of the associated molecule is long, conditions are favorable for such secondary reactions.

It is evident from Table I that the life of the associated molecule increases very rapidly with the value of q. It can be stated that in general a bimolecular association reaction will be of the second order, except those reactions in which the resultant molecule is of a very simple form.

The Double Minimum Problem Applied to the Ammonia Molecules[1]

F. T. WALL AND GEORGE GLOCKLER
University of Minnesota, Minneapolis, Minnesota
(Received December 26, 1936)

A simple quantum-mechanical calculation has been made to obtain the doublet separations for the parallel type frequencies of the ammonias. The calculated values for the separations are: NH_2D (21), NHD_2 (11) and ND_3 (5.8) cm^{-1}, which compare favorably with observed values: NH_2D (20), NHD_2 (10) and ND_3 (3.4) cm^{-1}.

THE symmetrical double minimum problem such as arises in the consideration of the vibrations of the ammonia molecule has been studied by a number of authors.[2] The treatment given by Manning was an exact one which he applied successfully to the molecules NH_3 and ND_3. In the present paper there will be outlined a simple although approximate method of treating the problem and the results will be applied to calculate the doublet separations for the molecules NH_2D, NHD_2 and ND_3. The particular mode of vibration here considered is that in which the nitrogen atom of the ammonia molecule oscillates through the plane of the hydrogens.

A simple potential energy function for such a double minimum problem is given by the expression

$$V=\tfrac{1}{2}k(|x|-l)^2,$$

where $2l$ equals the distance between the minima and k is a force constant. The corresponding potential energy curve consists of portions of two parabolas, and except for the sharp point in the middle, the function should represent fairly well the potential energy of an actual system (see Fig. 1). If we regard the sharp point as a perturbation to the true potential function whatever it may be, it is seen that its contribution to the total energy is small, because the wave functions are small in this region.

A particle subject to the above type of potential energy would behave in the neighborhood of the minima very much like a harmonic oscillator. Accordingly for the lowest pair of energy levels, the wave functions can be approximated by

$$\psi_{0\pm}=N_{0\pm}\{e^{-b(x-l)^2}\pm e^{-b(x+l)^2}\}.$$

The wave function with the positive sign is a symmetric function whereas that with the negative sign is an antisymmetric function. $N_{0\pm}$ is the normalizing factor and b, which for a harmonic oscillator equals $(\pi/h)(km)^{\frac{1}{2}}$, could be taken as a variation parameter. It was found in the calculations, however, that although varying b produced some lowering of the energy levels, very little difference was produced in the separations of the levels, so the above given value of b was retained throughout.

For the next lowest pair of energy levels, the wave functions assumed were

$$\psi_{1\pm}=N_{1\pm}\{(x-l)e^{-b(x-l)^2}\pm(x+l)e^{-b(x+l)^2}\},$$

where the positive sign now corresponds to the *antisymmetric* function and the negative sign to the *symmetric* function. Each of the symmetric functions is, of course, orthogonal to each of the antisymmetric ones, but any one of the functions

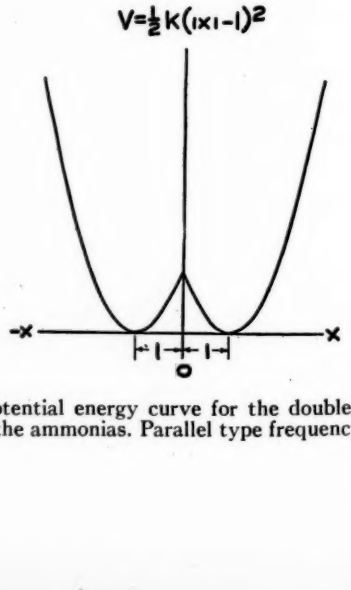

FIG. 1. Potential energy curve for the double minimum for the ammonias. Parallel type frequency ν_3.

[1] This article is based upon part of a thesis to be presented to the faculty of the Graduate School of the University of Minnesota by F. T. Wall in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Morse and Stueckelberg, Helv. Phys. Acta. **4**, 337 (1931); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); Rosen and Morse, Phys. Rev. **42**, 210 (1932); M. F. Manning, J. Chem. Phys. **3**, 136 (1935).

TABLE I.

COMPOUND	ν_0(mean)	q^2	a_0-s_0	a_1-s_1	$\Delta\nu$ (calc.)	$\Delta\nu$ (obs.)
NH_3	944.5 cm^{-1}	7.02	2.52 cm^{-1}	30.4 cm^{-1}	(33) cm^{-1}	33 cm^{-1}
NH_2D	884	7.51	1.49	19.5	21	20
NHD_2	813	8.16	.76	10.7	11	10
ND_3	747.5	8.88	.35	5.46	5.8	3.4

is not exactly orthogonal to the other function of the same symmetry. To make the orthogonality complete, one could add to $\psi_{1\pm}$ (without the normalizing factor) the term

$$\frac{\mp le^{-2bl^2}}{1\mp e^{-2bl^2}}\{e^{-b(x-l)^2}\mp e^{-b(x+l)^2}\}.$$

It turns out, however, that $2bl^2>7$ and hence the correction for complete orthogonality is very small. Such a refinement is unwarranted by the approximate nature of the problem and so the additional term was omitted.

The energies of the two pairs of lowest levels have been calculated by using the above functions and evaluating the integral

$$W=\int\psi H\psi d\tau,$$

$$H=-\frac{h^2}{8\pi^2m}\frac{d^2}{dx^2}+\tfrac{1}{2}k(|x|-l)^2.$$

Making the substitutions

$$b=(\pi/h)(km)^{\frac{1}{4}},\quad 2bl^2=q^2$$

and

$$1/2\pi(k/m)^{\frac{1}{4}}=\nu_0,$$

there result the following expressions for the energies:

$$W_{0S}=\frac{h\nu_0}{2}\left\{1+\frac{2q^2-4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn-4/(\pi)^{\frac{1}{2}}qe^{-q^2}}{1+e^{-q^2}}\right\},$$

$$W_{0A}=\frac{h\nu_0}{2}\left\{1+\frac{2q^2-4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn}{1-e^{-q^2}}\right\},$$

$$W_{1S}=\frac{3h\nu_0}{2}\left\{1+\frac{2q^2-4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn-4q^3/(\pi)^{\frac{1}{2}}e^{-q^2}}{3[1-(1-2q^2)e^{-q^2}]}\right\},$$

$$W_{1A}=\frac{3h\nu_0}{2}\left\{1+\frac{2q^2-4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn-8/(\pi)^{\frac{1}{2}}qe^{-q^2}+4q^3/(\pi)^{\frac{1}{2}}e^{-q^2}}{3[1+(1-2q^2)e^{-q^2}]}\right\}.$$

The subscripts S and A refer, respectively, to symmetric and antisymmetric states. The quantity q multiplied by $(1/2\pi)(h/\nu_0)^{\frac{1}{4}}$ represents half the "normal coordinate" separation of the minima.

The height of the potential hill is given by $V_{x=0}=(h\nu_0/2)q^2$. Assuming that this height is the same for each of the molecules NH_3, NH_2D, NHD_2 and ND_3, there is obtained a relationship between ν_0 and q, namely:

$$\nu_0q^2=\text{const.}$$

Using the mean values of the observed frequencies[3] and finding the value of q^2 that gives the correct separation for NH_3, it is then possible to compute the other separations. The results are given in Table I. The agreement of the calculated frequency differences $\Delta\nu$ is acceptable, while the calculation of the energy level differences (a_0-s_0) is not satisfactory in the case of ammonia (NH_3) where the experimental value[4] is 0.67 cm^{-1} in comparison with a calculated value of 2.52 cm^{-1}.

The calculated height of the potential hill is 3317 cm^{-1} which is about 50 percent too high since the actual function does not go up to a sharp point as here assumed. In addition to the errors introduced by the approximations made, there is some inaccuracy involved in assuming that the potential hill has the same height for each of the molecules. The height of the hill probably increases with increasing mass because the more massive particles will spread out less when the nitrogen atom penetrates the potential barrier. The effect of increasing the height would be to lower the calculated separation, a change which would be favorable especially in the case of ND_3.

[3] Migeotte and Barker, Phys. Rev. **50**, 418 (1936).

[4] Wright and Randall, Phys. Rev. **44**, 391 (1933).

The Nature of the Crystalline Fields Present in $Er_2(SO_4)_3 \cdot 8H_2O$

FRANK H. SPEDDING*
Chemical Laboratory of Cornell University, Ithaca, New York
(Received February 10, 1937)

The splitting of the basic state of $Er_2(SO_4)_3 8H_2O$ due to the presence of the crystalline fields was calculated according to the method of Van Vleck, and Penney and Schlapp. Assuming a cubic field, the basic state in the absence of a magnetic field should split into five levels with the relative separations 0, 19, 39, 85, 89 cm^{-1}. Meehan and Nutting have located them spectroscopically at 0, 19, 41 and 85. When the potential field constant D is assumed to be the same as experimentally determined for $Nd_2(SO_4)_3 \cdot 8H_2O$, then there are no arbitrary constants in the calculations, and the calculated over all splitting agrees with the values found within a few percent. If the true value of D could be used, the deviation would be even less. Similar calculations were made for $Dy_2(SO_4)_3 8H_2O$. While the calculated splitting is of the same order as that found experimentally, the agreement is not good. Reasons for the lack of agreement are given. The magnetic susceptibility expressions for both salts are given and the agreement with experiment in the case of Er is excellent.

THE atoms in a solid are so close together that they exert powerful electric fields on each other and these fields will cause a splitting of the energy states of the unperturbed atoms of the solid. The nature and magnitude of this splitting will depend, of course, on the various states present and on the symmetry and position of the surrounding atoms in the solid. This problem has been considered theoretically by a number of investigators, notably Bethe[1] and Van Vleck.[2] Penney and Schlapp,[3] using the methods of Van Vleck, have dealt with the specific cases of $Nd_2(SO_4)_3 8H_2O$ and $Pr_2(SO_4)_3 8H_2O$ in an article in which they treated the paramagnetic susceptibility of these salts theoretically. Although the salts are monoclinic, it was assumed by them that the field about the rare earth ion would be predominantly cubic due to the octahedron of oxygens about that ion. The potential of the electric field of the atoms surrounding the metallic ion was represented by a Taylor's expansion. This amounted to applying to the whole crystal the method of "the self-consistent field" and consequently neglected exchange effects between different crystal atoms. The dominant term in the potential for cubic fields is of the form $D(x^4+y^4+z^4)$ (except for a term $-3Dr^4$ which shifts all levels equally). All terms except this were neglected. They found that the basic state of Nd^{+++} which is a $^4I_{9/2}$ would split into three levels in the cubic field, the upper two being doubly degenerate so that there would be a further splitting if rhombic terms were present in the field. The solution of their secular determinant gave the following equations for the ten energy states,

$$W_1 = 20.95\,A + 1.833\,G + 0.3879\,G^2/A,$$
$$W_2 = 9.11\,A + 2.788\,G - 0.3411\,G^2/A,$$
$$W_3 = 9.11\,A - 0.542\,G + 0.1015\,G^2/A,$$
$$W_4 = -19.59\,A - 3.121\,G - 0.0468\,G^2/A,$$
$$W_5 = -19.59\,A + 1.542\,G - 0.1015\,G^2/A,$$

and five more obtained from these by changing the sign of G. Here $G = g\beta H$. From these they derived the expression for the susceptibility per gram atom,

$$\chi = (2g^2\beta^2 N/A)[(0.1483e^{19.59\mu} + 0.2396e^{-9.11\mu} - 0.3879e^{-20.95\mu}) + \mu(6.065e^{19.59\mu} 4.031e^{-9.11\mu} + 1.680e^{-20.95\mu})] \div (2e^{19.59\mu} + 2e^{-9.11\mu} + e^{-20.95\mu}) \quad \text{where} \quad \mu = A/kT.$$

They evaluated the constant A from the experimental magnetic susceptibility data of Gorter and de Haas[4] and obtained a value of $A = -20.6$ cm^{-1}. The theoretical curve of the variation of the susceptibility with temperature calculated from the above equation gave a beautiful fit with the experimental points. A

* Baker Research Fellow, Cornell University.
[1] Bethé, Ann. d. Physik **3**, 133 (1929).
[2] Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932); Phys. Rev. **41**, 208 (1932).
[3] Penney and Schlapp, Phys. Rev. **41**, 194 (1932); also footnote 2 of *ibid.* **42**, 666 (1932).
[4] Gorter and de Haas, Leiden Comm. 218b.

similar fit between theory and experiment was found for $Pr_2(SO_4)_3 8H_2O$. Unfortunately there were a number of discrepancies, e.g., the field constant D needed to give a fit for Nd was 3.9 times as large as the one used for Pr. This seems unreasonable when one considers that $Pr_2(SO_4)_3 \cdot 8H_2O$ and $Nd_2(SO_4)_3 8H_2O$ are so much alike crystographically and chemically that they can be distinguished from each other only with the greatest of difficulty. Also, when the method was applied to Sm, serious difficulties were encountered, for while the maximum number of levels permitted by theory was two in a cubic field or three in a rhombic field, Spedding and Bear[5] had definitely established spectroscopically that at least five low lying levels occurred. Further, the experimental evidence itself was not in a satisfactory state. The magnetic susceptibility measurements of Gorter and de Haas, while most complete with respect to temperature variation unfortunately do not agree with the room temperature values of a number of other investigators. Finally, all experimental evidence on the susceptibility of Er[6] seem to indicate that it obeys Curie's law over the whole temperature range. It would be very difficult to account for this behavior on the basis of the theory if the constant of the equations were great enough to account for the large deviations from Curie's law found by Gorter and de Haas for $Nd_2(SO_4)_3 8H_2O$.

In view of these difficulties Mr. Hamlin, Dr. Nutting and I investigated the energy states of $Nd_2(SO_4)_3 8H_2O$ spectroscopically. We did not find levels at 0, 243 and 834 cm^{-1} as calculated by Penney and Schlapp but did find them at 0, 77 and 260 cm^{-1}. The relative spacing of these levels is just that predicted by Penney and Schlapp, and if one evaluates their constants from our data, one obtains a value for A equal to -6.41 cm^{-1}. The calculated susceptibility does not pass through any of the experimental points of Gorter and de Haas, but does pass through the experimental points of S. Meyer,[7] Zernicke and James,[8] and others.[9]

The field constant D is only about one-third as large as calculated by Penney and Schlapp and therefore more in agreement with the Pr value.

While the magnetic susceptibility measurements are not very sensitive to a small rhombic term in the potential equation, the splitting of some of the levels is, and should be easily detected spectroscopically. We were unable to detect any splitting of these levels and were forced to conclude that if any rhombic terms existed they could not be more than two percent of the cubic term. This seems astonishing when one considers that the rare earth ions are situated in a monoclinic crystal and that even if the octahedron of oxygen about the ion gave a predominantly cubic field, the rest of the crystal should not give rise to an appreciable rhombic term.

On account of the above facts it seemed worthwhile to calculate the energy states and susceptibility expressions for Er^{+++} and Dy^{+++}. Er, being the complementary element to Nd on the other side of the rare earth group, has the same basic state except that it is inverted and has the largest J value instead of the smallest. $Nd^{+++} = 4f^3\ {}^4I_{9/2}$, $Er^{+++} = 4f^{(14-3)}\ {}^4I_{15/2}$, Dy^{+++} and Sm^{+++} occupy similar relative positions. $Sm^{+++} = 4f^5\ {}^6H_{5/2}$ $Dy^{+++} = 4f^{(14-5)}\ {}^6H_{15/2}$.

As the $\Delta\nu$'s are fixed by experiment, the only arbitrary constant in the equations is the field constant D. If this is determined by experiment for Nd it should be the same for Er. Therefore, if the assumptions regarding the nature of the potential field are valid, then one can calculate without any arbitrary constants whatsoever the nature and magnitude of the splitting of the basic state in Er^{+++}.

The calculation for Er^{+++} has been made by exactly the same method as that used by Penney and Schlapp in calculating the splitting of Nd^{+++}. The secular determinant consisted of 16 rows and columns. The matrix elements were

[5] Spedding and Bear, Phys. Rev. **46**, 975 (1934).

[6] Jackson, Phys. Soc. London, Sept. (1936), finds that the susceptibility of Er can be represented by the expression $\chi(T+6) = C$ where C is the Curie constant calculated according to Hund's method. de Haas, Wiersma and Cape (Leiden Commu. 201b) find a similar relation except that $\Delta = 1.5$ and C is somewhat lower. They state, however, that the absolute values are incorrect due to an error in calibration and they have promised to repeat this work. A number of other investigators have obtained the Hund value at room temperatures.

[7] S. Meyer, Physik. Zeits. **26**, 51, 478 (1925).

[8] Zernicke and James, J. Am. Chem. Soc. **48**, 2827 (1926).

[9] Selwood has summarized all results in his paper, J. Am. Chem. Soc. **55**, 3161 (1933).

calculated by means of the equations

$$\sum_i (x_i^4+y_i^4+z_i^4)(J, M; J, M) = K+pM^2\{7M^2+5-6J(J+1)\},$$

$$\sum_i (x_i^4+y_i^4+z_i^4)(J, M; J, M\pm 4) = \tfrac{1}{2}p[(J\mp M)!(J\pm M+4)!/(J\pm M)!(J\mp M-4)!]^{\frac{1}{2}},$$

which were derived in Penney and Schlapp's paper. The origin of the energy was chosen so as to avoid fractions. The secular determinant, fortunately, factored into four quartics. Only two of these required solving as the other two were identical with them due to the Kramers[10] degeneracy. (Kramers has shown that an electric field alone is not sufficient to remove the final twofold degeneracy of the levels.) Bethe has pointed out that the $^4I_{15/2}$ level splits in a cubic field into five levels. Thus three of the eight roots of the equations were repeating and were a great help in self-checking the results. The quartic equations were

$Er_2(SO_4)_3 8H_2O$

$$0=\begin{vmatrix} -W+(15/2)G+914a & 12\,a(13\cdot7\cdot5\cdot3)^{\frac{1}{2}} & 0 & 0 \\ 12\,a(13\cdot7\cdot5\cdot3)^{\frac{1}{2}} & -W+(7/2)G-3574a & 4\cdot5\cdot6\,a(11\cdot7\cdot3)^{\frac{1}{2}} & 0 \\ 0 & 4\cdot5\cdot6\cdot a(11\cdot7\cdot3)^{\frac{1}{2}} & -W-(1/2)G-94a & 3\cdot4\cdot5\cdot3a(11\cdot7)^{\frac{1}{2}} \\ 0 & 0 & 3\cdot4\cdot5\cdot3a(11\cdot7)^{\frac{1}{2}} & -W-(9/2)G-4774a \end{vmatrix}$$

$$0=\begin{vmatrix} -W+(13/2)G-3454a & 12\,a(13\cdot11\cdot7\cdot5)^{\frac{1}{2}} & 0 & 0 \\ 12\,a(13\cdot11\cdot7\cdot5)^{\frac{1}{2}} & -W+(5/2)G-2086a & 7\cdot8\cdot9a(5\cdot3)^{\frac{1}{2}} & 0 \\ 0 & 7\cdot8\,9a(5\cdot3)^{\frac{1}{2}} & -W-(3/2)G-814a & 60a(13\cdot11\cdot3)^{\frac{1}{2}} \\ 0 & 0 & 60a(13\cdot11\cdot3)^{\frac{1}{2}} & -W-(11/2)G-5014a \end{vmatrix}$$

$a=pD$, p being the coefficient in the matrix elements. Then the levels in the presence of the magnetic field are,

$$W_1=-5468.9a\mp 4.5819G-(0.003308/a)G^2,$$
$$W_2=-5468.9a\mp 2.8736G-(0.009505/a)G^2,$$
$$W_3=-4059.6a\pm 3.9805G-(0.003030/a)G^2,$$
$$W_4=-4059.6a\pm 1.6558G+(0.011307/a)G^2,$$
$$W_5=-2673.9a\pm 2.8332G+(0.005012/a)G^2,$$
$$W_6=+\ 834.4a\mp 0.2323G+(0.001314/a)G^2,$$
$$W_7=+\ 834.4a\pm 4.6311G-(0.063185/a)G^2,$$
$$W_8=+1166.1a\pm 2.5872G+(0.061346/a)G^2,$$

where $G=g\beta H$.

While as previously mentioned "a" can be directly calculated from pD, we shall first determine it from experiment and then compare it with the calculated result. Meehan and Nutting, of the University of California, have determined the splitting of the basic state of Er^{+++} in $Er_2(SO_4)_3 8H_2O$ spectroscopically and very generously have allowed me to use their data in advance of publication. They found levels at 0, 19, 41 and 85 cm^{-1}. If we fix "a" so that the two lowest levels are 19 cm^{-1} apart, then the other levels occur at 39, 85 and 89 cm^{-1}. Meehan and Nutting found 41 and 85. Transitions to the 89 level would be weak as the selection rules are unfavorable with regard to this level. Its statistical weight is only half that of the other levels, and what few transitions might occur from it would be easily confused with the 85 level since at liquid-air temperatures when these lines appear they are at least two or three wave numbers in width. They found no evidence of a rhombic field, for if one examines the constant energy differences by which they located their lines, one finds no evidence of splitting of the doubly degenerate levels. Again as in Nd the agreement with the experiment is much better than one would expect in view of the rather

[10] H. A. Kramers, Proc. Amst. Acad. **33**, 959 (1930).

drastic assumptions with regard to the form of the potential field equation.

The expression for the magnetic susceptibility takes the form

$$\chi=(2Ng^2\beta^2/a)[(+0.012813e^{+5468.9\mu}$$
$$-0.008277e^{+4059.6\mu}-0.005012e^{+2673.9\mu}$$
$$+0.061871e^{-834.4\mu}-0.061346e^{+11661})$$
$$+(a/KT)(14.6258e^{+5468.9\mu}+9.293175e^{+4059.6\mu}$$
$$+4.013618^{+2673.9\mu}+10.74986e^{-834.4\mu}$$
$$3.346937e^{-1166.1\mu})]\div[2e^{+5468.9\mu}+2e^{+4059.6\mu}$$
$$+e^{+2673.9\mu}+2e^{-834.4\mu}+e^{-1166.1\mu}]$$
$$\mu=ha/kT$$

and gives a curve which scarcely deviates from the Curie value in a $1/\chi$ *vs.* T, diagram. The deviation can be seen only on a large graph since even at 20°K it is less than 3 percent.[11]

The coefficient of the matrix element, p, was calculated by Penney and Schlapp to be $33q/91$. The value of q was also calculated by them for Nd. Using their method it was found that q for Er was the same as for Nd except that the sign was changed, thereby inverting the splitting pattern. Then $q=+"I"/32670$ where $"I"=\int_0^a r^6R^2(r)dr$ and where $R(r)$ is the radial wave function of one of the equivalent electrons. The quantity "I" is independent of J, L, M, S but it does depend on the total quantum number and the effective nuclear charge. Therefore "a" can be expressed in terms of known constants. Thus, for Nd,

Experimental values

$$-0.286\ \text{cm}^{-1}=a=p_{9/2}D=\frac{-2380}{1001\times32670}I_{\text{Nd}}D.$$

For Er

$$0.0135\ \text{cm}^{-1}=a=p_{15/2}D=\frac{33\,I_{\text{Er}}\,D}{91\times32670}.$$

Since the D is assumed to be the same in such similar salts, the ratio of the $a_{\text{Er}}/a_{\text{Nd}}=C\times(I_{\text{Er}}/I_{\text{Nd}})$, where C is the constant determination from the above equation. The resulting value of $I_{\text{Er}}/I_{\text{Nd}}$ is 0.31.

As the "I" 's for the two salts are identical except for the screening constants, one can write $(Z_{\text{Er}}-\sigma)^4/(Z_{\text{Nd}}-\sigma)^4=I_{\text{Nd}}/I_{\text{Er}}$, since everything but these two factors cancels out. Z is equal to the atomic number of the element in question and σ is the screening constant calculated according to the method of Slater[12] (allowing one for S, P and D electrons and 0.35 for F electrons). If a for Nd is regarded as a known quantity -0.286 cm^{-1}, this formula gives $a=0.0112$ cm^{-1} for Er which compares very favorably with $a=0.0135$ cm^{-1}, the value found experimentally since the screening constants are not known to very high accuracy. It should be noted that while one has a slight leeway in the over-all separation of the multiplet since the values of the screening constants are not accurately known, the relative splitting of the levels is fixed once the potential function is determined. It would perhaps be better to calculate the screening constants for this type of calculation from the above data than *vice versa* and I hope to be able to check such calculations when we obtain more data on other salts later.[13]

Since the secular determinant and therefore the splitting pattern is independent of L and S and depends only on J and M, the splitting pattern of $Dy^{+++}(^6H_{15/2})$ will be the same as for Er^{+++}. It will be inverted, however, since the q is negative ($q=-I/10395$). The coefficient of the matrix element (p) calculated according to the method of Penney and Schlapp is $(14/91)q$. Thus the levels should occur in the ratio 0, 8, 90, 123, 156 and occur about those positions. Meehan and Nutting, however, report levels at 0, 22, 57 (80, 112) which while of the right magnitude are not in good agreement with calculations. This is not surprising, however, when one recalls that in Sm, the companion element, Spedding and Bear found too many levels for the simple theory. If these levels are electronic

[11] The same expression would hold for D_y^{+++} if the levels had occurred where predicted except the a would be negative.

[12] Slater, Phys. Rev. **36**, 1 (1930).

[13] Assuming Slater's value of 1 for s, p and d electrons and calculating the screening constant of the $4f$ electron from the a constants determined, one obtains 0.44 instead of 0.35. This deviation is not large and, moreover, it is in the right direction for we have made the assumption that the field constant D is constant for both salts. This is not strictly true. The size of the Nd ion is larger than the Er and this causes a slightly larger unit cell for Nd thereby making the D slightly smaller. The increased size of the unit cell is reflected in the crystal structure, for in the homologous series of the rare earth sulphates, when the ion has reached the size of La^{+++} an extra water enters the lattice and we obtain $La_2(SO_4)_3 9H_2O$.

as I have maintained, they would be expected to perturb the calculated levels. While these extra electronic levels in Dy would not be so close, they would still be present and would be expected to perturb the other levels to a greater or less extent, thereby destroying the validity of the simple calculations.

The agreement of experiment with Penney and Schlapp's theory for Er and Nd is very much better than one has any right to expect when one considers the very simple assumptions which were made when they set up the expression for the potential function. The agreement with Dy is not good but the disagreement is easily accounted for.

I am extending the experimental work in this field to a large number of salts of as many rare earths as I can obtain and hope to find out shortly whether or not this remarkable agreement continues to persist. I wish to express my indebtedness to Professor Kirkwood who has taken a keen interest in this problem and who spent considerable time discussing with me the theoretical side of the subject.

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The Influence of Dipole-Dipole Coupling on the Specific Heat and Susceptibility of a Paramagnetic Salt

J. H. Van Vleck,
Harvard University, Cambridge, Massachusetts

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The mutual magnetic potential energy of atomic magnetic dipoles is unimportant in salts of high dilution at ordinary temperatures, but becomes important in determining the temperature scale in the new very low region obtained by magnetic cooling. This "dipole-dipole" energy is not to be confused with exchange interaction which is important in concentrated magnetic materials and which is there responsible for ferromagnetism at ordinary temperatures. The partition function, and hence the entropy, specific heat, and susceptibility are calculated for a paramagnetic solid inclusive of dipole and simultaneously also feeble exchange coupling. In Sections 3–4 the computation is made for atoms otherwise free, but in Section 6 they are subjected in addition to a crystalline Stark field. Comparison with experiment is made in the following paper by Hebb and Purcell. Our method of partition functions is to be contrasted with the usual, essentially static Lorentz method of representing dipole-dipole coupling by a local field, e.g., $H+4\pi M/3$ for a long test body. The Lorentz procedure is shown to be only a first approximation, which is really warranted if the density is so low or the temperature so high that one may neglect all terms but the first in the development of the partition function in $1/T$. Otherwise the usual results of the local field method are obtained only by an extrapolation which is comparable with the assumption in Heisenberg's theory of ferromagnetism of identical energy for all states with the same crystalline spin. Two other types of extrapolation, based on a second approximation, are obtained which correspond respectively to assuming a Gaussian distribution of energies for these states and to use of the local field proposed by Onsager. The latter seems to be much the more satisfactory of the two.

1. Introduction

THE purpose of the present paper is to calculate the partition function for an ensemble of atoms, each of which carries a magnetic moment, and is subject to both (a) an applied magnetic field and (b) coupling with the moments of other atoms. In Section 6 we shall include simultaneously (c) a crystalline potential of the type used by Bethe, Kramers, Penney and Schlapp, etc.[1] We shall be concerned primarily with media of high magnetic dilution, where the interaction (b) is due mainly to the usual magnetic potential energy of two dipoles, which varies as the inverse third power of their distance of separation. Exchange effects have usually been considered unimportant in media of high magnetic dilution because they fall off exponentially with distance. However, Kramers[2]

[1] For a general discussion of the influence of crystalline fields on magnetic susceptibilities, exclusive of dipole-dipole interaction, see J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Chap. XI; also especially the subsequent work of Penney and Schlapp, Phys. Rev. **41**, 194; **42**, 666 (1932), summarized in Chap. X of Stoner's *Magnetism and Matter*.

[2] H. A. Kramers, Physica **1**, 182 (1933).

has shown that because of a complicated coupling via the excited states of intermediate, normally nonmagnetic atoms, the diminution may be sometimes less drastic than exponential. Hence we shall make our computations general enough so that (b) can include some exchange as well as true magnetic coupling.

After the partition function Z per unit volume has been calculated, there are a variety of applications, especially in connection with the production of very low temperatures by the magnetic method, which will be discussed in the following paper by Hebb and Purcell.[3] The specific heat is given by the relation

$$c_v=\frac{\partial}{\partial T}\left(kT^2\frac{\partial \log Z}{\partial T}\right), \tag{1}$$

while the free energy F and entropy S are supplied by[4]

$$F=-kT\log Z, \quad S=-\partial F/\partial T. \tag{2}$$

The formula for the magnetic moment per unit volume is

$$M=kT\partial \log Z/\partial H_0, \tag{3}$$

where H_0 is the applied magnetic field *before insertion of the test body*. The quotient of M to H_0 we shall call the experimental susceptibility. It is to be distinguished from the susceptibility as usually defined in electrodynamics which is the ratio of M to the field H inside the test body *after* its insertion. The passage from one kind of susceptibility to the other requires the use of "demagnetizing corrections" giving the relation between H_0 and H. Unfortunately H cannot be measured directly, whereas H_0 is usually known from the dimensions of the solenoids, etc.

2. The Hamiltonian Function, and Expansion of the Partition Function

Let μ_i be the magnetic moment of atom i, and let V_i be its crystalline potential, which is a function of the coordinates of all the electrons of the atom. However, those with vanishing angular momentum enter only in a trivial fashion, merely introducing an additive constant in V_i. The Hamiltonian function is

$$\mathfrak{H}=\sum_i V_i+\sum_{j>i} w_{ij}-H_0\sum_i \mu_{zi}, \tag{4}$$

with

$$w_{ij}=r_{ij}^{-3}[\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j-3(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})/r_{ij}^2]+V_{ij}^{ex}. \tag{5}$$

Here $\mathbf{r}_{ij}$ is the radius vector connecting atoms i and j, and r_{ij} is the modulus of $\mathbf{r}_{ij}$. We suppose throughout that H_0 is directed along the z axis. The first part of (5) represents the dipole-dipole coupling between atoms i and j, while the last term is the exchange energy. Usually one is interested in an atom for which only one multiplet component is effective, so that one can take

$$\boldsymbol{\mu}_i=g\beta\mathbf{J}_i, \tag{6}$$

where $\mathbf{J}_i$ is the angular momentum vector of the atom, measured in multiples of $h/2\pi$, while β is the Bohr magneton $he/4\pi mc$, and g is the Landé factor. If we forget orbital valence, assuming that the exchange integral connecting an electron of atom i and one of j has a value K independent of how the orbital angular momentum of either electron is oriented, and if all electrons not in closed shells are equivalent, then it can be shown[5] that apart from an additive constant

$$V_{ij}^{ex}=v_{ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j/r_{ij}^3, \tag{7}$$

where

$$v_{ij}=-\frac{2r_{ij}^3}{g^2\beta^2}\left[\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right]^2 K. \tag{8}$$

Here S, L, and J are, respectively, the spin, azimuthal, and inner quantum numbers of an atom. The atoms of the crystal are to be considered all alike when free, so that it is not necessary to attach subscripts to S, L, and J. The factor $r_{ij}^3/g^2\beta^2$ is included in (8) in order to make v_{ij} dimensionless and facilitate the formal

[3] M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 338 (1937).

[4] Our free energy F is in a certain sense analogous to the Gibbs rather than Helmholtz definition, as we have $dF=-SdT-MdH$ rather than $-SdT+HdM$.

[5] Eqs. (7–8) are well-known consequences of the Dirac vector model when $J=S$, $L=0$. See, for instance, Dirac, Proc. Roy. Soc. **123A**, 714 (1929) or Chap. XII of the writer's *Electric and Magnetic Susceptibilities*. The bracketed factor in (8) owes its existence to the fact that only the component of S along J is effective when $L\neq 0$ provided nondiagonal elements in J are neglected. It is squared because one must make the projection along J for both atoms involved in any given coupling term.

simultaneous handling of dipole-dipole and exchange interaction. It is seen that the two types of interaction, though physically quite different are mathematically rather similar, since both couple together the angular momentum vectors of different atoms. The exchange effect, however, is isotropic, as it depends only on the relative orientation of $\mathbf{\mu}_i$ and $\mathbf{\mu}_j$, and not on the inclination of either relative to $\mathbf{r}_{ij}$. If the exchange coupling is not direct, but via the excited states of intermediate atoms, an apparent rather than true value is to be used for the exchange integral K.

In most cases important in the production of very low temperatures, the atom is effectively in an S state, so that in (6–7–8) etc. one can take $J=S$, $L=0$. One then often speaks of the dipole-dipole coupling as spin-spin interaction, as in the following paper by Hebb and Purcell. In many instances, notably in gadolinium compounds or in those containing manganous or ferric ions, the paramagnetic ingredient is actually in an S state, while in other examples furnished by salts of the iron group, the orbital angular momentum is quenched by the crystalline field, leaving us only the spin to consider.

The partition function is

$$Z=\sum_\lambda \exp\,(-W_\lambda/kT) =\sum_\lambda\left\{1-\frac{W_\lambda}{kT}+\frac{W_\lambda^2}{2k^2T^2}-\cdots\right\}, \quad (9)$$

where the sum is over all the states of the crystal, regarded as a single unit. Eq. (9) may also be written

$$Z=\eta\left[1-\frac{\mathcal{H}_{\rm Av}}{kT}+\frac{(\mathcal{H}^2)_{\rm Av}}{2k^2T^2} -\frac{(\mathcal{H}^3)_{\rm Av}}{6k^3T^3}+\frac{(\mathcal{H}^4)_{\rm Av}}{24k^4T^4}+\cdots\right], \quad (10)$$

where η is the total number of states. The precise value of η is of no interest in connection with specific heat or susceptibility, as (1) and (3) do not depend upon η since η is independent of H_0 or T. The subscript Av denotes a quantum-mechanical mean value, in other words the diagonal sum or spur divided by the total number of rows or columns in the matrix representing $\mathcal{H}$. Now in virtue of the invariance of the spur, this average can be calculated in any system of representation. This fact is a tremendous aid in problems of the present sort, as Waller has already shown.[6] It obviates the necessity of determining the characteristic values W_λ of $\mathcal{H}$, a practically hopeless task, and enables us to use systems of representation appropriate to one individual atom. Consequently we can use the familiar system which diagonalizes the component m_{zi} of angular momentum of each atom i in the direction of the applied field, even though m_{zi} is not really a constant of the motion because of perturbations due to dipole-dipole and exchange coupling between atoms.

Our development (9) or (10) of the partition function as a series in $1/T$ is obviously applicable only if the temperature is not too low. An alternative method of approximation valid in the vicinity of $T=0$ is being investigated by Professor H. A. Kramers.

Each member of (10) can be developed as an ascending series in the field H_0. From considerations of symmetry there will be no odd powers of H_0 so that

$$Z=Z^0(1+Z^{(2)}H_0^2+\cdots). \quad (11)$$

Throughout the paper, zero superscripts imply absence of the applied magnetic field, whereas zero subscripts imply absence of the material or of its dipole-dipole interaction.

3. Calculation of Z^0 and the Specific Heat for Atoms not Exposed to Crystalline Fields

Usually one is interested in the specific heat and entropy in the absence of applied field, so that in connection with (1) and (2) it suffices to determine the portion Z^0 of the partition function which persists when $H_0=0$. In the present section we shall hence compute Z^0, deferring until Section 4 the determination of $Z^{(2)}$ which is needed for the susceptibility. For simplicity, the crystalline potential terms V_i will be omitted until Section 6.

With $H_0=V_i=0$, one has

$$\mathcal{H}=\sum_{j>i}w_{ij}, \quad (12)$$

[6] I. Waller, Zeits. f. Physik **79**, 370 (1932).

where by (5), (6) and (7)

$$w_{ij}=g^2\beta^2 r_{ij}^{-3}[(1+v_{ij})(\mathbf{J}_i\cdot\mathbf{J}_j) -3(\mathbf{J}_i\cdot\mathbf{r}_{ij})(\mathbf{J}_j\cdot\mathbf{r}_{ij})/r_{ij}^2]. \quad (13)$$

The average of the expression (13) can be taken over atoms i and j independently since the complete diagonal sum factors into the diagonal sum for individual atoms. Furthermore

$$(J_{xi})_{\mathrm{Av}}=(J_{yi})_{\mathrm{Av}}=(J_{zi})_{\mathrm{Av}}=0, \quad (14)$$

as is obvious from symmetry considerations or from the fact that positive and negative values of the magnetic quantum number can be matched in pairs. Hence

$$\mathfrak{IC}_{\mathrm{Av}}=0. \quad (15)$$

Terms in $\mathfrak{IC}^2$. To compute the quadratic term in (10), one uses, besides (14), the relations

$$0=(J_{xi}J_{yi})_{\mathrm{Av}}=(J_{yi}J_{xi})_{\mathrm{Av}}=\cdots=(J_{zi}J_{xi})_{\mathrm{Av}};$$
$$(J_{xi}^2)_{\mathrm{Av}}=(J_{yi}^2)_{\mathrm{Av}}=(J_{zi}^2)_{\mathrm{Av}}=\tfrac{1}{3}J(J+1). \quad (16)$$

The reader should be careful to distinguish between $\mathbf{J}_i$ and J. The former is a vector matrix, whereas the latter is the usual inner quantum number, which is by hypothesis the same for all atoms. On the other hand the spatial components J_{xi}, J_{yi}, J_{zi} vary from atom to atom.

On performing the spatial averaging of the direction cosines and using (13), (14), (16), one finds that

$$(\mathfrak{IC}^2)_{\mathrm{Av}}=(\textstyle\sum_{j>i}w_{ij})^2_{\mathrm{Av}}=\sum_{j>i}(w_{ij}^2)_{\mathrm{Av}}$$
$$=\tfrac{1}{2}N\textstyle\sum_j(w_{ij}^2)_{\mathrm{Av}}=\tfrac{1}{6}g^4\beta^4J^2(J+1)^2N^2Q, \quad (17)$$

where N is the number of atoms/cc and

$$Q=N^{-2}\textstyle\sum_j r_{ij}^{-6}(2+v_{ij}^2). \quad (18)$$

The most important contribution to the sum (18) comes from the coupling between adjacent atoms. If all other interactions are disregarded and each atom is surrounded by z neighbors at equal distances r, (18) becomes

$$Q=zr^{-6}N^{-2}(2+v^2), \quad (19)$$

where v is the value of v_{ij} connecting adjacent atoms. For cubic arrangements, the dipole-dipole part of (18) may readily be summed accurately. If one neglects exchange except between neighbors, then one finds

$$Q_{sc}=12(1.40+\tfrac{1}{2}v^2), \quad Q_{fc}=12(1.20+\tfrac{1}{2}v^2),$$
$$Q_{bc}=(256/27)(1.53+\tfrac{1}{2}v^2). \quad (20)$$

If dipole-dipole forces are included only between neighbors, the factors 1.40, 1.20, 1.53, are replaced by unity. The subscripts *sc*, *bc*, *fc* refer, respectively, to the simple, body, and face centered cube structures.

Terms in $\mathfrak{IC}^3$. We now proceed to the terms in $\mathfrak{IC}^3$. Here there are two types of terms. One kind arises because $(w_{ij}^3)_{\mathrm{Av}}\neq 0$ inasmuch as

$$(J_{xi}J_{yi}J_{zi})_{\mathrm{Av}}=-(J_{yi}J_{xi}J_{zi})_{\mathrm{Av}}=\tfrac{1}{2}i(J_{zi}^2)_{\mathrm{Av}}=\tfrac{1}{6}iJ(J+1). \quad (21)$$

Formulas (21) are consequences of the relations

$$J_{xi}J_{yi}-J_{yi}J_{xi}=iJ_{zi}, \quad \text{etc.} \quad [(J_{xi}J_{yi})_{\mathrm{Av}}+(J_{yi}J_{xi})_{\mathrm{Av}}]=0, \quad (22)$$

which are well-known commutation rules or else are readily established by partial integration of the angular momentum operator integrals. Eqs. (21) give the only type of nonvanishing third-order term in w_{ij}^3, since

$$(J_{xi}^3)_{\mathrm{Av}}=(J_{xi}^2J_{yi})_{\mathrm{Av}}=(J_{xi}J_{yi}J_{xi})_{\mathrm{Av}}=0, \quad \text{etc.} \quad (23)$$

Thus one finds that

$$(w_{ij}^3)_{\mathrm{Av}}=\tfrac{1}{3}g^6\beta^6J^2(J+1)^2r_{ij}^{-9}(1+\tfrac{3}{2}v-\tfrac{1}{2}v^3). \quad (24)$$

Another contribution to the mean of $\mathfrak{IC}^3$ comes from products of the form $w_{ij}w_{jk}w_{ki}$. The mean of such products is sensitive to the type of geometrical arrangement or symmetry in the crystal. We now make the restriction that the crystal be a simple cube as far as the spacing of paramagnetic ions is concerned. The most important terms of the present sort are then those in which two of the w's in the triple product relate to coupling between adjacent atoms, while the third involves atoms separated by an amount $\sqrt{2}r$. In other words, the three atoms i, j, k form the three corners of an isosceles right-angle triangle. In calculating the mean value of any individual product, one must allow for the fact that r_{ij} has different directions for the various sides of the triangle. Hence

$$w_{ij}w_{jl}w_{li}=[\beta^6g^6/r^9(\sqrt{2})^3][(1+v)J_{xi}J_{xj}+(1+v)J_{yi}J_{yj}+(v-2)J_{zi}J_{zj}][(1+v)J_{xj}J_{xk}+(v-2)J_{yj}J_{yk}+(1+v)J_{zj}J_{zk}]$$
$$\times[J_{xk}J_{xi}-(J_{yk}+J_{zk})(J_{yi}+J_{zi})+\tfrac{1}{2}(J_{yk}-J_{zk})(J_{yi}-J_{zi})]. \quad (25)$$

Here, we have supposed, for simplicity, but without loss of generality, that the y and z axes are directed along the two

legs of the triangle. Also we have included exchange coupling only between neighbors, i.e. along the two short sides of the triangle. This approximation is warranted if the exchange interaction diminishes much more rapidly with distance than does the dipole-dipole. Using (16), one finds that

$$(w_{ij}w_{jk}w_{ki})_{\mathrm{Av}}=[3\beta^6g^6/r^9\sqrt{2}^3][\tfrac{1}{3}J(J+1)]^3(1+v). \tag{26}$$

In connection with (24), it will suffice to consider only the coupling between neighbors, as (24) involves $J(J+1)$ to a lower power than does (26), and so need not be evaluated especially accurately. With this approximation, there are $3N$ terms of the type (24). There are $72N$ terms of the triangular form assumed in (26). There are also many other triangular ones in which one or both of the two shorter sides of the triangle do not connect adjacent atoms. Their effect is calculated in a fashion analogous to (25–6) and it is found that with the simple cubic arrangement the effect of including all the larger triangles is the same as though they were neglected, and the $72N$ terms of type (26) each increased by a factor approximately $(1.3+1.3v)/(1+v)$. Thus one finds

$$(\mathfrak{IC}^3)_{\mathrm{Av}}=Ng^6\beta^6J^2(J+1)^2r^{-9}(1+\tfrac{3}{2}v-\tfrac{1}{2}v^3)+2N\sqrt{2}g^6\beta^6r^{-9}J^3(J+1)^3(1.3+1.3v). \tag{27}$$

Terms in $\mathfrak{IC}^4$. The fourth-order term $\mathfrak{IC}^4$ in (13) involves nonvanishing terms of three types, *viz.* $w_{ij}^2w_{kl}^2$, w_{ij}^4, and $w_{ij}^2w_{il}^2$, where it is to be supposed that all atoms denoted by different letters are distinct, i.e. $i\neq l$, etc. Clearly

$$(w_{ij}^2w_{kl}^2)_{\mathrm{Av}}=(w_{ij}^2)_{\mathrm{Av}}(w_{kl}^2)_{\mathrm{Av}}=[\tfrac{2}{3}g^4\beta^4J^2(J+1)^2]^2r_{ij}^{-6}r_{kl}^{-6}(1+\tfrac{1}{2}v^2)^2 \tag{28}$$

since the mean of w_{ij}^2 has already been computed in connection with (17).

A rather long calculation shows that

$$(w_{ij}^4)_{\mathrm{Av}}=\frac{g^8\beta^8J^4(J+1)^4}{r^{12}}\left[\frac{24}{25}(1+v_1)-\frac{16}{25}\frac{(1+v_1)}{J(J+1)}+\frac{11}{25}\frac{(1+v_2)}{J^2(J+1)^2}\right], \tag{29}$$

where v_1, v_2 are terms due to exchange, whose explicit values are

$$24v_1=-16v+36v^2+5v^4, \qquad 33v_2=28v+12v^2+10v^4. \tag{30}$$

The mean values needed in obtaining the result (30) are supplied by

$$(J_{z_i}^4)_{\mathrm{Av}}=\left[\frac{J^2(J+1)^2}{5}\right]\left[1-\frac{1}{3J(J+1)}\right], \qquad (J_{z_i}^2J_{z_i}^2)_{\mathrm{Av}}=\frac{1}{15}J^2(J+1)^2+\frac{1}{30}J(J+1), \tag{31}$$

The terms in (30) with $J(J+1)$ in the denominator arise from the noncommuting property of angular momentum, which requires us to observe carefully the ordering of products in the factors, as by (21) and (22) the corrections for noncommutation give contributions which do not average to zero.

If we include only coupling between neighbors, the terms in $w_{ij}^2w_{jl}^2$ are of two types, *viz.*, those in which atoms ijk are on the same straight line, and those in which r_{ij} forms an angle of 90° with r_{jl}. One-fifth of the terms are of the former and four-fifths of the latter type. When the two types are weighted in this fashion, one finds

$$(w_{ij}^2w_{jk}^2)_{\mathrm{Av}}=(32/75)Ng^8\beta^8J^4(J+1)^4r^{-12}[1-\tfrac{3}{4}(J^2+J)^{-1}](1+v_3), \tag{32}$$

where $v_3=(75v^4+252v^2+48v)/288$.

Now $\mathfrak{IC}^4$ is composed of $9N(3N-11)$ terms of structure (28), $3N$ of the type (29) and $90N$ of the class (32). This is all on the assumption that we consider only coupling between neighbors. A rough allowance for the interaction between non-neighbors can be made by multiplying the dipole-dipole parts (i.e., parts independent of v) of (28) and (32) by 1.4^2. The reason for this statement is that the multiple sums encountered can almost be factored into two sums of the form (18), for which the cubic non-neighbor correction factor is 1.4.

When one utilizes (15), (18), (27), (28), (29), (32), together with the remarks in the preceding paragraph on the structure of $\mathfrak{IC}^4$, one finds that if one stops with fourth-order terms, the partition function (10) becomes[7]

$$\begin{aligned}Z^0=\eta\Bigg\{1+N\frac{\tau^2}{T^2}(1.4+\tfrac{1}{2}v^2)-\frac{N\tau^3}{T^3}\left[\frac{(2+3v-v^3)}{12J(J+1)}+\frac{\sqrt{2}(1.3+1.3v)}{3}\right]+\frac{N^2\tau^4}{2T^4}(1.4+\tfrac{1}{2}v^2)^2\\ +\frac{N\tau^4}{T^4}\left[-\frac{11}{6}(1.4+\tfrac{1}{2}v^2)^2+\frac{3}{25}(1+v_1)-\frac{2}{25}\frac{(1+v_1)}{J(J+1)}+\frac{11}{200}\frac{(1+v_2)}{J^2(J+1)^2}\right.\\ \left.+\frac{8}{5}\left(1-\frac{1}{3J(J+1)}\right)(1.4+v_3)^2\right]+\cdots\Bigg\}.\end{aligned} \tag{33}$$

[7] Although (33) involves the square of N explicitly, only the first power appears in F or c_v (cf. Eq. (35)), except implicitly through τ, as F is of the form $(aN+bN^2+\cdots)/(1+cN+\cdots)$ with $c=+b/a$.

Here it has been convenient to introduce a characteristic temperature τ defined by

$$\tau = g^2\beta^2 NJ(J+1)/k. \quad (34)$$

The specific heat corresponding to (33) can immediately be obtained from (1). If, to make the formulas short, we neglect exchange and hence set $v=0$, and if we assume that J is a large number, then (1) becomes

$$c_v = Nk[2.8(\tau/T)^2 - 3.7(\tau/T)^3 - 4.0(\tau/T)^4 + \cdots]. \quad (35)$$

It is to be cautioned that this formula is only valid for a simple cubic arrangement. However, the coefficient of the first term is adapted to any arrangement by replacing 2.8 by $\frac{1}{6}Q$, where Q is given in (18). This first term in c_v has also been computed independently by I. Waller,[8] and to this approximation our results and methods are identical with his. With the face and body centered cubic arrangements, it can be shown that the coefficient of τ^3/T^3 becomes, respectively, 3.4 and 3.5 instead of 3.7. The remaining term, in τ^4/T^4, is subordinate if the temperature is high enough that the convergence is good, and then not much harm will be done in using the simple cubic arrangement for this term even if the actual crystalline arrangement is different. Unfortunately, one is often interested in temperatures comparable with the characteristic temperature τ. Under such circumstances, (35) cannot be used, as the higher order terms in τ^5/T^5 etc., omitted in (35) would surely come into play. If we were to use (35) as it stands without additional terms, one could obtain something so fantastic as a negative total specific heat by taking τ/T sufficiently large! Under such circumstances, it is probably better to stop with the first term of (35). This procedure is equivalent to replacing $(\mathfrak{H}^{2n})_{Av}$ by $[(2n!)/n!2^n]\,[(\mathfrak{H}^2)_{Av}]^n$, $(\mathfrak{H}^{2n+1})_{Av}$ by zero, and has a certain resemblance to the approximations in Heisenberg's theory of ferromagnetism[9] in its simplest form, which on the whole nevertheless work surprisingly well. In fact, in the following paper by Hebb and Purcell, where comparison is made with experiment, it is found that the agreement is usually better if one uses only the first term rather than the complete expression (35). A possible extrapolation of (35) by means of the Onsager model is discussed at the very end of the present article.

The characteristic temperature τ defined in (34) has a simple physical interpretation, as follows. In classical theory, the dipole-dipole interaction is represented by the artifice of taking the local field acting upon the molecule to be $H_0+\Phi M$ rather than H_0. The extra part ΦM arises from two causes: (I) The macroscopic field H in the test body is not the same as the field H_0 before its insertion. The portion of Φ arising from this source is negative, and its absolute value is often called the demagnetizing coefficient.[10] (II) There is the correction because of the fact that in a solid any given atom is in a privileged position, so that the field at the atom is not the same as the mean field. Instead in a body with cubic symmetry the atom may be regarded as at the center of a spherical cavity, and by a well-known argument, Lorentz[11] showed that the resulting contribution to Φ is $4\pi/3$. The value of Φ resulting from the two combined causes is shape dependent; with a spherically molded body Φ vanishes, a very long slab placed parallel to the field yields $\Phi=4\pi/3$, while for a very wide body $\Phi=-8\pi/3$, provided in each case the atoms are on the average cubically spaced. If the effective field acting upon the moment is $H_0+\Phi M$, and if saturation is neglected, the familiar quantum-mechanical version of the Langevin formula[12] for the moment is

$$M = [g^2\beta^2 NJ(J+1)/3kT][H_0+\Phi M]; \quad (36)$$

whence by (34)

$$M = \tfrac{1}{3}\tau H_0/(T-\tfrac{1}{3}\Phi\tau). \quad (37)$$

Clearly, except for a factor $\frac{1}{3}\Phi \leqq 4\pi/9$, our characteristic temperature τ is the same as the "Curie" temperature at which formula (37) fails due to zero denominator and at which it is necessary to consider saturation, so that ferromagnetism sets in. Numerically τ is very small ($\sim 0.05°$K), as is obvious from the fact that

[8] I. Waller, Zeits. f. Physik **104**, 132 (1936).
[9] For a description of Heisenberg's theory of ferromagnetism see, for instance, his original paper, Zeits. f. Physik **49**, 619 (1928) or reference 17.
[10] An excellent discussion of demagnetization corrections is given in Stoner, *Magnetism and Matter*, pp. 38–40.
[11] Cf. H. A. Lorentz, *The Theory of Electrons*, note 54.
[12] See, for example, p. 285 of reference 10.

Curie temperatures of ordinary size are obtained in the Weiss theory[13] only by artificially giving Φ enormous values ($\sim 10^5$) rather than taking $\Phi \leqq 4\pi/3$.

It is to be noted that our formula (35) for specific heat is independent of shape, unlike that (36) for moment. The reason is that the expression Q defined in (18) and any other grating sums encountered in the derivation of (35) involve only inverse sixth or other high negative powers of the interatomic distance and so are practically independent of boundary conditions, whereas this is not true of Φ, which involves a sum of inverse third powers (cf. later Eq. (43)).

4. Calculation of $Z^{(2)}$ and the Susceptibility for Atoms not Exposed to External Fields

In the present section we shall consider only the ordinary susceptibility for fields not powerful enough to cause saturation, and so it will suffice to compute the coefficient $Z^{(2)}$ in the development (11). If in (10) we neglect terms beyond the fourth order in $\mathfrak{H}$, this coefficient has the value

$$Z_2^{(2)} = \eta Z_0^{-1}\left[\frac{(a^2)_{\mathrm{Av}}}{2k^2T^2} - \frac{p(aab)_{\mathrm{Av}}}{6k^3T^3} + \frac{p(aabb)_{\mathrm{Av}}}{24k^4T^4}\right] \quad (38)$$

with the abbreviations

$$a = -\sum_i J_{zi} g\beta H_0, \quad b = \sum_{j>i} w_{ij}, \quad (39)$$

and with w_{ij} as in (5). The symbol p means that in averaging, all possible orders of the factors in the following product are to be used; e.g.

$$paab = \tfrac{1}{3}(a^2b + aba + ba^2). \quad (40)$$

It is necessary to distinguish between the various orders because a and b do not commute in multiplication.

The first term of (38) is simply the usual magnetic part of the partition function obtained by disregarding the interaction between elementary magnets. Use of (16) gives immediately

$$(a^2)_{\mathrm{Av}}/2k^2T^2 = NH_0^2g^2\beta^2J(J+1)/6k^2T^2. \quad (41)$$

To evaluate the next term in (38), we note that $J_{zi}J_{zj}J_{qk}J_{ql}$ vanishes on the average unless the subscripts coincide in pairs, and unless in addition $q=z$ rather than $q=x, y$. The nonvanishing form is $J_{zi}J_{zj}J_{zi}J_{zj} = J^2(J+1)^2/9$. These statements are also valid even if the order of the factors is permuted. Thus one finds[14]

$$p(aab)_{\mathrm{Av}} = \tfrac{2}{3}H_0^2g^4\beta^4J^2(J+1)^2 \times \sum_{j>i}[1+v_{ij}-3\cos^2(z, r_{ij})]/r_{ij}^3. \quad (42)$$

Let us set

$$\Phi = -N^{-1}\sum_j[1-3\cos^2(z, r_{ij})]/r_{ij}^3. \quad (43)$$

Then $M\Phi$ is the z component of the field at atom i due to a grating constructed by placing a dipole of strength M/N at each atom j of the crystal (except $j=i$) with axis always parallel to the field H, i.e., to the z axis. Hence Φ as defined by (43) is the same as the factor Φ in the customary local field $H+\Phi M$ discussed preceding Eq. (36).[15] In particular, in a spherically molded cubic crystal Φ vanishes, since the mean value of $\cos^2(H, r_{ij})$ in (43) is 1/3. This agrees with the fact in such a body the demagnetizing and Lorentz corrections cancel. In a nonspherical specimen, one cannot take this mean value equal to 1/3, as atoms near the boundary make an important contribution to the sum (43), and spoil the symmetry.

The exchange terms presumably vary much more strongly with distance than in the inverse third fashion. Hence, to a sufficient approximation, we can regard v_{ij} as having a nonvanishing value v only when it connects adjacent atoms, so that $\sum_j v_{ij}/r_{ij}^3 = vz'N$ where $z' = z/Nr^3$ and where z is the number of neighbors possessed by any atom. For a simple cubic arrangement z and z' are identical.

When we use (43) and the above simplification of the exchange terms, (42) becomes

$$p(aab)_{\mathrm{Av}} = -\tfrac{1}{3}NH_0^2g^4\beta^4J^2 \times (J+1)^2[N\Phi - Nvz']. \quad (44)$$

If we retain only the part of (38) through aab, i.e., through $\mathfrak{H}^3$ in (10), Eqs. (38), (41), (44) and

[13] A convenient summary of the Weiss theory is given on p. 352ff. of reference 10.

[14] A factor 2 appears on the right side of (42) because of the two possibilities $i=k$, $j=l$, or $i=l$, $k=j$. This factor disappears in (44) because ij and ji count as one term in a double sum such as (42), so that there are $N/2$ single sums of the form (43).

[15] That essentially the same results will be obtained with discrete grating sums such as (43) as with the classical Lorentz continuum, as long as there is isotropy, has been demonstrated by Ewald, Ann. d. Physik **49**, 1 (1916).

(34) show that the formula (3) for the moment gives

$$M=(\tau H/3T)[1+\tfrac{1}{3}(\Phi-z'v)\tau T^{-1}]. \quad (45)$$

To first powers of Φ this formula is, apart from exchange corrections equivalent to (37), as one sees by expanding (37) as an ascending series in Φ. Thus to linear terms in Φ, the treatment by means of the partition function agrees with the method of the local field. To see whether this similarity also holds to Φ^2, we must now proceed to examine the fourth order (i.e., $\mathfrak{H}\mathcal{C}^4$) part of the partition function. Before so doing we must caution that even the expressions of the first degree in Φ are rigorous only for ellipsoidal test bodies, as only bodies of such shape have a uniform polarization and so admit a constant demagnetizing factor or in other words a value of the sum (43) independent of the position of atom i. Actually, cylinders are often used experimentally, and the best that one can do is to approximate them by ellipsoids. Because of other difficulties (e.g., insufficiency of Eq. (37) when we come to higher powers of Φ) the resulting error is probably not usually of paramount concern. The exchange corrections are seen to have the effect of replacing Φ by $\Phi-z'v$. Eq. (8) shows that v has the opposite sign from the exchange integral K. Hence if the latter is negative, as in most nonferromagnetic materials, the exchange terms have the effect of decreasing the apparent value of Φ, or in other words a demagnetizing tendency. In ferromagnetic media, on the other hand, K is positive and large because of high magnetic density. Under these conditions exchange is in the present first approximation equivalent to an enormous positive value of Φ, as in the Weiss theory of the molecular field.

Terms in $\mathfrak{H}\mathcal{C}^4$. By (38–39), the fourth degree position of the partition involves

$$\eta p(aabb)_{\mathrm{Av}}/24Z^0k^4T^4=(\eta g^2\beta^2/Z^0k^4T^4)p[\tfrac{1}{2}\textstyle\sum_{j>i}(J_{zi}J_{zj}w_{ij}w_{ij})_{\mathrm{Av}}+\tfrac{1}{2}\sum_{j>i}(J_{zi}J_{zi}w_{ij}w_{ij})_{\mathrm{Av}}$$
$$+\tfrac{1}{4}(N-2)(J_{zk}{}^2)_{\mathrm{Av}}\textstyle\sum_{j>i}(w_{ij}{}^2)_{\mathrm{Av}}+\sum_{j>i}\sum_{k(\neq i)}(J_{zi}J_{zk}w_{ij}w_{jk})_{\mathrm{Av}}], \quad (46)$$

where k is not to equal i or j, and p has the same meaning as in (40). On using (16), (21), (31) and taking care to include all possible orderings of the noncommutative factors, one finds after some calculation that

$$p\textstyle\sum_{j>i}(J_{zi}J_{zj}w_{ij}w_{ij})_{\mathrm{Av}}=-Ng^4\beta^4[J(J+1)/6]^2\cdot\tfrac{1}{3}\sum_j r_{ij}{}^{-6}(v_{ij}{}^2-1), \quad (47)$$

$$p\textstyle\sum_{j>i}(J_{zi}J_{zi}w_{ij}w_{ij})_{\mathrm{Av}}=(N/18)g^4\beta^4[J^3(J+1)^3-\tfrac{1}{3}J^2(J+1)^2]\sum_j(v_{ij}{}^2+2)/r_{ij}{}^6, \quad (48)$$

$$(J_{zk}{}^2)_{\mathrm{Av}}\textstyle\sum_{j>i}(w_{ij}{}^2)_{\mathrm{Av}}=\tfrac{1}{2}g^4\beta^4N[\tfrac{1}{3}J(J+1)]^3\sum_j(3v_{ij}{}^2+6)/r_{ij}{}^6, \quad (49)$$

$$p\textstyle\sum_{j>i}\sum_{k(k\neq i)}(J_{zi}J_{zk}w_{ij}w_{jk})_{\mathrm{Av}}=\tfrac{1}{2}[\tfrac{1}{3}J(J+1)]^3Ng^4\beta^4[(-N\Phi+Nvz')^2-\sum_j r_{ij}{}^{-6}(2+v_{ij}{}^2)]. \quad (50)$$

The derivation of (50) requires some comment, as here the spatial averaging is complicated by exclusion of $k=i$, which prevents easy factorization. However, one can add and subtract the term $k=i$. Thus one can write, with the aid of (16)

$$\textstyle\sum_{j>i}\sum_{k(k\neq i)}(J_{zi}J_{zk}w_{ij}w_{jk})_{\mathrm{Av}}=\tfrac{1}{2}[\tfrac{1}{3}J(J+1)]^3Ng^4\beta^4[\{(\sum_j r_{ij}{}^{-3}f_{ij})_{\mathrm{Av}}\}\{\sum_k(r_{jk}{}^{-3}f_{jk})_{\mathrm{Av}}\}$$
$$-\textstyle\sum_j(r_{ij}{}^{-6}f_{ij}{}^2)_{\mathrm{Av}}], \quad (51)$$

where $f_{ij}=[1+v_{ij}]-3\cos(z,r_{ij})[\cos(x,r_{ij})+\cos(y,r_{ij})+\cos(z,r_{ij})]$ and where on the right side the sum includes $k=i$. In (51) it is possible to average separately, i.e., replace the average product by the product of averages, because after the inclusion of $k=i$ there is no statistical correlation between the directions of r_{ij} and r_{jk}. In the first part of the right side of (51), convenient use may be made of the definition (43) of Φ and the relations $0=\sum_j r_{ij}{}^{-3}\cos(x,r_{ij})\cos(y,r_{ij})$, etc. which are consequences of the fact that the Lorentz local field is parallel to the direction z of the applied field, at least in an isotropic body. The exchange contributions are simplified as after Eq. (43). In the last part of (51) one may take

$$[\cos^2(x,r_{ij})]_{\mathrm{Av}}=\tfrac{1}{3},\quad [\cos(x,r_{ij})\cos(z,r_{ij})]_{\mathrm{Av}}=0,\quad [\cos(x,r_{ij})\cos^3(z,r_{ij})]_{\mathrm{Av}}=0,\quad \text{etc.} \quad (52)$$

provided the crystal has cubical symmetry, or provided we desire only the powder susceptibility if the arrangement is not cubic. This condition we suppose to be met. Use of (52) is then allowed regardless of the shape of the body, since the last part of (51) involves inverse sixth powers of the distance and so boundary conditions do not enter. For similar reasons, relations such as (52) can be used in obtaining (47–48–49). In view of all the above, (51) finally can be thrown into the form (50).

Substituting (47–50) in (46) and using (41–42), one finds that the partition function (38) becomes

$$Z^{(2)}=(\tau/6kT^2)[1+\gamma T^{-1}+\gamma^2T^{-2}-\delta T^{-2}], \quad (53)$$

where τ, Q are defined as in (34), (18) and

$$\gamma=\tfrac{1}{3}\tau(\Phi-vz'), \quad \delta=xQ\tau^2/9. \quad (54)$$

with

$$x=1+[(3+3v^2zr^{-6}N^{-2}Q^{-1})/(8J^2+8J)]. \quad (55)$$

In obtaining (53) we have used the explicit value of $1/Z^0$, which by (33) or (10–15–17) to the present degree of approximation is

$$1/Z^0=\eta^{-1}[1+\tfrac{1}{3}Q(\tau/2T)^2]^{-1}=\eta^{-1}[1-\tfrac{1}{3}Q(\tau/2T)^2].$$

By (3) and (11), the moment is $M=2kTZ_2H$. Hence we can write

$$M=\tfrac{1}{3}H\tau/(T-\gamma+\delta T^{-1}), \quad (56)$$

since to the present stage of approximation there is no distinction between $1+\gamma T^{-1}+\gamma^2T^{-2}$ and $1/(1-\gamma T)$ or between $1-\delta T^{-2}$ and $1/(1+\delta T^{-2})$.

Reference to (37) shows that if we omit δT^{-1}, Eq. (56) is exactly what one gets by taking the local field to be $H+(\Phi-vz')M$. The presence of the last term δT^{-1}, however, shows that it is not accurate to represent the dipole-dipole interaction by means of the customary local field. We must, of course, examine whether the modifications due to this extra term are appreciable. Clearly it is unimportant if the actual temperature T is large compared with the characteristic temperature τ. This condition is met in paramagnetic salts except at very low temperatures. In the electric case, the analogous correction term can be important even at room temperatures, as we will discuss in another paper. Even with paramagnetic substances of fairly high magnetic dilution, the influence of the last term is by no means negligible in the celebrated experiments at Leiden and elsewhere on the production of very low temperatures. In the case of $Gd_2(SO^4)8H_2O$, for instance, τ equals 0.19°K. If we neglect exchange, doubtless warranted at this magnetic dilution, and assume a spherically molded body, so that $\Phi=0$, the effect of the extra term is to make the moment at $T=\tau$ less than half as large as it would be otherwise.

5. Comparison with Heisenberg's Gaussian Calculation and Onsager's Method. Can Dipole-Dipole Coupling Ever Produce Ferromagnetism?

Of course, as soon as the temperature is so low that our new term in (56) is important, there is immediately the difficulty that the whole series development is not convergent. There are many different formulas which agree with ours to the degree of accuracy of the the calculation, but which would yield completely different results when T is comparable with τ. For instance, we might omit the last term from the denominator of (56) and add $-\frac{1}{3}H\tau\delta/T^3$ to its right side. Our reason for writing our result in the form (56) is that (56) has a form analogous to that obtained in Heisenberg's theory of ferromagnetism when a Gaussian distribution of energy values is assumed. In fact, (56) agrees exactly with Heisenberg's Gaussian formula (except for his saturation terms) when one neglects everything but exchange,[16] and takes $J=\frac{1}{2}$, the case considered by him.

The derivation of a formula substantially equivalent to (56) may also be made in a completely different way. Instead of our computation by series development of the partition function, one may attempt a calculation by Heisenberg's method in which in the first approximation all states belonging to the same magnetic quantum number M' for the entire crystal are regarded as having the same energy, and in which in the second approximation a Gaussian distribution is assumed for these states. (It is usually stated that identity or else Gaussian distribution of energies is assumed for all states with the same total angular momentum J' for the whole crystal. However, corresponding assumptions can equally well be made for

[16] When only exchange is included, Φ vanishes. Also then the factor x defined in (55) reduces to $1+\frac{3}{4}(J^2+J)^{-1}$, as Q becomes $N^{-2}zr_0^{-6}v^2$.

all states with the same M', since owing to the enormity of J' the overwhelming fraction of states with a given J' have M' nearly equal to J' when $H\neq 0$.) The difference as compared with Heisenberg's original calculations is, of course, that we must include dipole-dipole rather than just exchange coupling. There is immediately one difficulty, as in our problem the total dipole-dipole interaction energy $\sum_{i>i} w_{ij}$ does not commute either with $M'=\sum J_{zi}$ or with $J'^2=(\sum J_{xi})^2+(\sum J_{yi})^2+(\sum J_{zi})^2$. Hence one cannot really talk about the states belonging to a given value of M' or J'. This is one reason why we presented the calculation in the way we have, rather than by a method analogous to Heisenberg's, since the latter thus cannot be applied at all rigorously to our problem. Our other reasons are that our scheme of series development of the partition function presents an interesting alternative to the Heisenberg procedure, and especially that, unlike the latter, it need not be specialized to $J=\frac{1}{2}$ as soon as the calculation is extended beyond the first or nonspreading approximation. If, nevertheless, as close a parallel as possible with Heisenberg is desired, the mean energy, mean square energy, etc. may formally be evaluated for a given M' and J', in the sense that these means are taken proportional to the appropriate matrix spur or diagonal sum. We shall not give the details of the calculation. They are made by means of the vector model, after a manner explained elsewhere.[17] If identity of energy for all states of a given M' is assumed, and if saturation effects are disregarded inasmuch as we are considering only weak fields, a formula is found which is exactly the same as (56) except that the last term δT^{-1} in the denominator is missing. This is just what one would expect to be true. To obtain this term, it is necessary to go to the second approximation, in which a Gaussian spread of energies for a given M' is assumed. Here there is the usual difficulty that with present mathematical machinery[18] it is possible to make the calculation only with $J=\frac{1}{2}$. With such a specialization the computation can be carried through, and one obtains a formula not quite identical with (56). The difference is only that the definition (55) of x becomes $x=1+[(-3+9zv^2r^{-6}N^{-2}Q^{-1})/8(J^2+J)]$. The cause of this slight discrepancy is, however, not hard to find. The Heisenberg method is really applicable only when $\sum J_{zi}g\beta H$ commutes with the rest of the Hamiltonian function. Therefore to obtain an expression comparable with that furnished by his procedure, one ought erroneously to write all the b terms in front of the a (or *vice versa*) in (38), or in other words omit the operator p. When this change is made, the results by the two methods are similar.

In order to have ferromagnetism, it is necessary for the denominator of (56) to vanish for a real value of T. The resulting value of T, which may be called the Curie temperature, is

$$T_c=\tfrac{1}{6}\tau(\Phi-vz)\pm\tfrac{1}{6}\tau[(\Phi-zv)^2-4Qx]^{\frac{1}{2}}. \quad (57)$$

[17] See Chap. XII of the writer's *Electric and Magnetic Susceptibilities*.

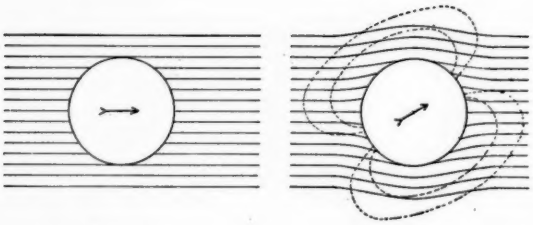
[18] Cf. footnote, p. 329 of reference 17.

Let us consider the case of no exchange, i.e., $v=0$, since the possibility of ferromagnetism resulting from exchange has already been dealt with by Heisenberg. If $J=\infty$, i.e., $x=1$, Eq. (20) shows that for a simple cubic arrangement (57) is real if and only if $\Phi\geqq 8.2$. For the face-centered and body-centered cube, the corresponding inequalities are both $\Phi\geqq 7.6$. Even larger values of Φ are required if J is finite. Now from the mode of definition, the maximum value of Φ that can occur physically in an isotropic material is that $4\pi/3=4.2$ appropriate to a very long test body. Hence if formula (56) is granted, dipole-dipole interaction is never adequate to produce ferromagnetism. This is a quite different result than if one represents this interaction by means of a local field $H_0+\Phi M$, as then ferromagnetism sets in at the temperature $\frac{1}{3}\Phi\tau$ (cf. Eq. (37)).

We thus conclude that according to (56) no plausible arrangement of atoms is sufficient to give ferromagnetism from dipole-dipole effects alone. The situation is consequently different from that in the usual ferromagnetism due to exchange. Here Heisenberg found that if $J=\frac{1}{2}$ there could be ferromagnetism even with a Gaussian distribution provided $z>8$ and the exchange integral has the proper sign. This result can also be seen[16] by omitting all of (57) except the terms involving v. Of course one can question whether the Gaussian approximation is a good one. In the case of ordinary, i.e., exchange ferromagnetism, it is known that a formula where all the states of the same spin are regarded as having the same energy works better empirically than the more elaborate expression based on the Gaussian approximation. A partial theoretical explanation has been given by Fay,[19] who was able to take into account half the spin-spin interactions rigorously, and thus found formulas agreeing well with those obtained by the nonspreading approximation. Extension of this method to the dipole-dipole coupling is, however, not feasible.

The second order or fluctuation effects are entirely ignored by using the usual Lorentz or Weiss local field, and are undoubtedly overrecognized in formulas like (56) based on a Gaussian distribution. However, these effects

[19] C. H. Fay, Proc. Nat. Acad. Sci. **21**, 537 (1935).



Lorentz Onsager

FIG. 1. In the Lorentz method, the field inside the cavity is computed on the assumption that the lines of induction outside the cavity are unmodified by the existence of the latter. With the Onsager model, the distribution of these lines is revised by elementary electrostatics to take cognizance of the cavity. The resulting portion of the local field may be called the direct part. In addition, Onsager has a "reaction field" which is shown by dashed lines in the figure and which arises because the dipole itself will polarize the surrounding medium. The direct and reaction contributions to the local field are given by the first and second terms of our later Eq. (85). The reaction field on the dipole is clearly always parallel to it and has no influence on the latter's orientation. So in dealing with permanent rather than induced polarization, only the direct portion need be considered. Eq. (58) is thus obtained by taking the moment M equal to the product of the polarizability $\psi/4\pi$ and the first member of (85), and then solving for M. In the case of induced polarization, the elementary dipoles are all parallel to the field, and the sum of Onsager's direct and reaction fields is identical with the Lorentz expression.

are considerably more important in the dipole-dipole than in the exchange case. In the latter, raising z from 6 to 8 was sufficient to give ferromagnetism even in a Gaussian calculation,[20] but with dipole-dipole forces, the values of Φ which would be necessary are far too large to be permissible even if $z=12$. The physical basis for this situation is not hard to see. In the dipole-dipole case, the mean energy is relatively small. In fact, for a spherically molded specimen it is exactly zero. Hence, the mean square of the dipole-dipole energy can be radically different from the square of the mean, and the fluctuation corrections correspondingly important.

Onsager's method.—Another, entirely different approach to the problem has been given recently by Onsager.[21] The gist of his observations is that the usual Lorentz field is not the best possible choice of a local field in an essentially static method. The reason is that the ordinary procedure assumes that the lines of force are the same outside the classical spherical cavity as though this cavity did not exist. Actually there will be a "back-action" of the dipole at the center of the cavity on the surrounding medium, and this effect will depend on how the given dipole is aligned. The distinction between the Lorentz and Onsager models is illustrated in Fig. 1. Onsager thus derives a new local field which is claimed to be a better approximation than the usual one. For further details, the reader is referred to his interesting paper.[21] It leads to the formula

$$M=(3/16\pi)H[-1+\psi+(1+\tfrac{2}{3}\psi+\psi^2)^{\frac{1}{2}}]$$
$$=(H/4\pi)[\psi+\tfrac{1}{3}\psi^2-(1/9)\psi^3-(1/27)\psi^4+\cdots], \quad (58)$$

with

$$H=H_0+\tfrac{1}{3}(3\Phi-4\pi)M, \quad \psi=4\pi N\mu^2/3kT. \quad (59)$$

The difference between H_0 and H simply represents the "demagnetizing correction," H_0 and H being respectively fields before and after insertion of the sample. This distinction is not discussed in Onsager's paper, as he considered dielectric media, but the adaptation to magnetic rather than electric dipoles is immediate. To make a fair comparison with (56), we must assume that the dipoles are distributed continuously rather than discretely. Then, apart from exchange corrections, (18) becomes

$$Q=8\pi N^{-1}\int_a^\infty r^{-4}dr=2(4\pi/3)^2 \quad (60)$$

as the volume of the classical cavity is to be chosen equal to the mean volume associated with an atom (or molecule), giving $1/N=4\pi a^3/3$. If we use (60), development of (56) gives the same series as (58) to terms in ψ^3 inclusive, provided we neglect exchange terms and provided we replace the noncommutation correction factor x by unity. It is not clear how either of the two latter effects could be introduced into Onsager's formula, since his *modus operandi* is entirely classical. The usual Lorentz procedure would give $\psi+\frac{1}{3}\psi^2+(1/9)\psi^3+\cdots$. The Onsager field is thus seen to be a better approximation than the Lorentz one at least if ψ is not too large.

[20] Incidentally, the present calculation shows as a corollary that in the ferromagnetic case of exchange rather than dipole-dipole coupling, Heisenberg's conclusion that use of a Gaussian spread prevents ferromagnetism is only true when $J=\frac{1}{2}$. Namely, as soon as one uses $J=1$ in (57) and omits all but exchange terms, one can still have a real positive Curie temperature even when $z=6$. Heisenberg obtained the same result, but his calculations were voided (reference 18) by an error which makes use of his group methods impossible when $J>\frac{1}{2}$.

[21] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

The physical arguments in Onsager's paper gave one good reason to expect this, but at the same time it is reassuring to have examined the situation analytically by use of the partition function. In this connection it is to be emphasized that (56) is only rigorous to ψ^3 and so the comparison cannot be made to a higher approximation. Onsager, of course, did not claim complete accuracy for his result.

The Onsager formula (58) agrees with the Gaussian one (56) in predicting that dipole-dipole interaction can never give ferromagnetism. Furthermore, (58) demands that the moment always increases as the temperature is lowered. With (56) this is unfortunately not true, since (56) has a maximum at $T=\sqrt{\delta}$. We thus believe that Onsager's formula is better than one based on a Gaussian distribution. Distinct experimental evidence that (58) or even (37) works better than (56) is given in the following paper of Hebb and Purcell.

To summarize, it must at present be regarded as uncertain theoretically whether or not ferromagnetism can result from dipole-dipole coupling. Alternative methods of calculation better suited to the vicinity of $T=0$ are greatly to be desired, which would decide whether or not the state of lowest energy is magnetic. The Bloch-Slater method applies unfortunately only for the exchange case. In dielectrics the analog of ferromagnetism does not occur nearly so often as (37) would demand, as we will discuss in a paper in a later issue of this journal. There are some magnetic experiments on long test bodies, notably $FeNH_4(SO_4)_2 12H_2O$ at which no ferromagnetism is found at temperatures considerably below the critical temperature at which (37) fails. However, Hebb and Purcell find that this difficulty practically disappears when one includes the effect of the crystalline field (i.e. uses our later Eq. (83) rather than (37)) which greatly lowers the susceptibility and hence the Curie temperature in the local field model. There are certain salts at which residual magnetization is found at very low temperatures, though rather curiously often no saturation curvature in weak fields.[22] Eq. (37) would predict both effects and (56) or (58) neither! All told, the actual behavior is probably intermediate between (37) and (58). This situation seems comprehensible, since the continuum model basic to (58) involves an excessively high value of Q. Namely (60) is over twice as large as any of the estimates (20) appropriate to discrete arrangements, and so (58) may over-accentuate the corrections to the Lorentz expression.

6. Calculation for Atoms Subject to Crystalline Fields

We shall now compute the specific heat and magnetic susceptibility for an ensemble of atoms subject to a crystalline field in addition to the applied external field and the dipole-dipole interaction.

Let us choose a system of representation which diagonalizes the energy of an individual atom subject to the crystalline and the applied fields. The matrix elements of the magnetic moment of atom i in this scheme, which are Hermitean, will be denoted by

$$\mu_{xi}(m_i; m_i'), \quad \mu_{yi}(m_i; m_i'), \quad \mu_{zi}(m_i; m_i'). \tag{61}$$

We suppose the applied field along the z axis. The letter m_i symbolizes the totality of quantum numbers which come into play for atom i. Therefore m_i includes a "crystalline quantum number" which determines the spatial orientation of the atom, but which is not the same as the ordinary magnetic quantum number unless the field has axial symmetry. In addition m_i contains the inner quantum number if several multiplet components are excited. The determination of the matrix elements (61) has been discussed in detail by Penney and Schlapp,[1] and need not be considered explicitly here. The point which we would like to stress here is that the calculation of these elements involves the solution of a "one-atom problem," and so is tractable by direct methods involving solution of algebraic equations of low degree. On the other hand we must use perturbation theory to

[22] N. Kürti, P. Lainé, Bernard-Vincent Rollin and F. Simon, Comptes rendus **202**, 1576 (1936); **204**, 675, 754 (1937). By the absence of saturation curvature we mean the failure of additional remanence to appear in feeble fields as long as they exceed 7 gauss.

handle the dipole-dipole interactions. Their influence has not been included in (61), and can only be treated by successive approximations, inasmuch as the dipole-dipole forces couple together the enormous number of atoms in the crystal, thereby spoiling the factorization into one-atom problems.

The characteristic values of the energy of atom i for the unperturbed problem will be denoted by $W_i(m_i)$. The total unperturbed energy of the crystal is then

$$W_M=\sum_i W_i(m_i). \tag{62}$$

To simplify printing, we omit attaching zero subscripts to the amplitudes μ_i and energies W_i, but it is nevertheless to be understood that they are throughout to be calculated in the unperturbed system of representation, i.e., exclusive of dipole-dipole coupling. Note that our unperturbed system is inclusive of portions, *viz.* crystalline and applied fields, which are usually regarded as belonging to the perturbing potential. Instead, the latter consists solely of the dipole-dipole and exchange energy, and therefore takes the form $\sum_{j>i} w_{ij}$ where (cf. Eq. (5) or (13))

$$w_{ij}(M;\,M')=w_{ij}(m_im_j;\,m_i'm_j')=r_{ij}^{-3}\sum_{q,\,q'=x,\,y,\,z}[(1+v_{ij})\delta(q;\,q') -3\cos(q,\,r_{ij})\cos(q',\,r_{ij})]\mu_{qi}(m_i;\,m_i')\mu_{q'j}(m_j;\,m_j'). \tag{63}$$

To the second approximation in the dipole-dipole coupling, i.e., to the second order in $(1/r_{ij}^3)$, the partition function is

$$Z=Z_0[1+A+B+\cdots], \tag{64}$$

where

$$Z_0=\sum_M \exp(-W_M/kT)=[\sum_{m_i}\exp(-W_i(m_i)/kT)]^N, \tag{65}$$

$$A=A^0+A^{(2)}H_0^2+\cdots=-(1/kTZ_0)\sum_M\sum_{j>i}w_{ij}(M;\,M)\exp(-W_M/kT), \tag{66}$$

$$B=B^0+B^{(2)}H_0^2+\cdots=(1/2k^2T^2Z_0)\sum{}''_{M,\,M'}\sum_{j>i}w_{ij}(M;\,M')\sum_{l>k}w_{kl}(M';\,M)\exp(-W_M/kT) +(1/kTZ_0)\sum{}'_{M,\,M'}\{\sum_{j>i}w_{ij}(M;\,M')\sum_{l>k}w_{kl}(M';\,M)/(W_{M'}-W_M)\}\exp(-W_M/kT). \tag{67}$$

Here Z_0 denotes the partition function in the absence of dipole-dipole coupling. It is not to be confused with Z^0, as Z^0 includes this coupling, but not the applied field, while the reverse is true of Z_0. In writing (66–7) we have utilized the fact that the amplitudes, energies, etc. and hence A, B can be developed as power series in H_0. The letter M denotes the totality of quantum numbers for some state of the entire crystal, and so comprises N times as many quantum numbers as m_i.

The equality signs and primes attached to the summations over M' require some explanation. They denote, respectively, inclusion and exclusion of those values of M' for which $W_M=W_{M'}$ (or in the later Eq. (72), those m_i', m_j' for which $W_i(m_i)+W_j(m_j)=W_i(m_i')+W_j(m_j')$). The situation $W_M=W_{M'}$ can arise primarily because of resonance degeneracy. Clearly the energy will be unaffected if we de-excite one atom and excite another one by the same amount. In other words, a partition $W_i(m_j)+W_j(m_i)$ between atoms i and j carries the same total energy as $W_i(m_i)+W_j(m_j)$.

For proof of (64), the reader is referred to a paper by R. Serber.[23] Eq. (64) can also be established by substituting in (9) the usual formulas for the second order perturbed energy, provided the perturbing potential λH_1 is taken as $\sum_{j>i}w_{ij}$. Eq. (64) is then obtained when one expands the exponentials in the partition function to terms of the order λ^2. There is, however, one simplification when working with the partition function rather than individual energy levels. Namely, it is not necessary to worry about the resonance degeneracy difficulties associated with the possibility of atoms trading quantum numbers. These difficulties enter in connection with the determination of the characteristic values of the energy even in the first approximation. However, because of the invariance of the spur, there is no trouble in constructing the partition function, and it is not necessary for us to solve the secular problem connected with resonance degeneracy.

[23] R. Serber, Phys. Rev. **43**, 1011 (1933), especially first form of his Eq. (13).

In virtue of (62), (65), and the first part of (63), Eqs. (66)–(67) may be written

$$A=-k^{-1}T^{-1}\sum_{j>i}(w_{ij})_{\mathrm{Av}},$$

$$B=\tfrac{1}{2}k^{-2}T^{-2}\{\sum_{ijkl}(w_{ij})_{\mathrm{Av}}(w_{kl})_{\mathrm{Av}}+2\sum_{ijk}(w_{ij}w_{jk})_{\mathrm{Av}}\}_{j>i,\ l>k(i,\ j\neq k,\ l)}+\alpha, \quad (68)$$

with
$$(w_{ij})_{\mathrm{Av}}=d_id_j\sum_{m_im_j}w_{ij}(m_im_j;\ m_im_j)\exp\left[-(W_i(m_i)+W_j(m_j))/kT\right], \quad (69)$$

$$(w_{ij}w_{jk})_{\mathrm{Av}}=d_id_jd_k\sum_{m_im_jm_k}[2kT\sum\nolimits'_{m'j}w_{ij}(m_im_j;\ m_im_j')w(m_j'm_k;\ m_jm_k)/(W_j(m_j')-W_j(m_j)$$
$$+w_{ij}(m_im_j;\ m_im_j)w_{jk}(m_jm_k;\ m_jm_k)]\exp\left[-(W_i(m_i)+W_j(m_j)+W_k(m_k))/kT\right], \quad (70)$$

$$d_i=1/\sum_{m_i}\exp\left[-W_i(m_i)/kT\right], \quad (71)$$

$$\alpha=\alpha^0+\alpha^{(2)}H^2+\cdots=\tfrac{1}{2}k^{-2}T^{-2}\sum_{i>j}d_id_j\sum\nolimits''_{m_im_jm'_im'_j}|w_{ij}(m_im_j;\ m_i'm_j')|^2\exp\left[-(W_i(m_i)\right.$$
$$\left.+W_{i,}(m_j))/kT\right]+k^{-1}T^{-1}\sum_{j>i}d_id_j\sum\nolimits'_{m_im_jm'_im'_j}\{|w_{ij}(m_im_j;\ m_i'm_j')|^2/(W_i(m_i')+W_j(m_j')$$
$$-W_i(m_i)-W_j(m_j))]\exp\left[-(W_i(m_i)+W_j(m_j))/kT\right]. \quad (72)$$

In (68), we are to exclude values of k and l which are equal to either i or j, whereas this exclusion was not made in (67).

Calculation of Z^0 and the specific heat.—First we will consider the form of the partition function in the absence of the applied field H_0, and so deal with the portions Z^0, A^0, B^0 of Z, A, B. In computing (64), (65), (68) we may, of course, then use the moment matrix elements and the energies appropriate to $H_0=0$, which we may denote by $\mu_{qi}{}^0(m_i;\ m_i')$, $W_i{}^0(m_i)$ $(q=x,\ y,\ z)$. Now to every state with a given value of the moment, there exists in general a state of equal and opposite moment with the same energy as long as no external field is applied, and as long as the crystalline field has a center of symmetry at each atom, which we shall suppose to be the case. Thus we have

$$\sum_{m_i}\mu_{qi}{}^0(m_i;\ m_i)\exp\left[-W_i{}^0(m_i)/kT\right]=0. \quad (73)$$

Eq. (72) for α is perfectly general. The various atoms need not be alike, and in particular can differ in the size and orientations of their crystalline fields—a not unusual situation since staggered arrangements are common in crystals. If we assume that all atoms are equivalent, i.e. have similar crystalline fields, then the subscripts i, j can be omitted from W, μ, d, etc. If, for simplicity, we further suppose that directions of r_{ij} are either oriented at random, or else that the paramagnetic ions are spaced in a simple, body or face-centered cubic field, without, however, the crystalline field necessarily having cubic symmetry, then we find

$$\alpha^0=\tfrac{1}{4}N^3Qk^{-2}T^{-2}d^2\sum_{q=x,\ y,\ z}\{[\sum_{m_i}\mu_q{}^0(m_i;\ m_i)^2\exp\left(-W^0(m_i)/kT\right)]^2$$
$$+\sum_{m_im_j(m_i\neq m_j)}|\mu_q{}^0(m_i;\ m_j)|^4\exp\left[-(W_i{}^0(m_i)+W_j{}^0(m_j))/kT\right]$$
$$+2kT\sum\nolimits'_{m_im_jm'_im'_j}[|\mu_q{}^0(m_i;\ m_i')|^2|\mu_q{}^0(m_j;\ m_j')|^2/(W_i{}^0(m_i')-W_j{}^0(m_j')$$
$$-W_i{}^0(m_i)-W_j{}^0(m_j)]\exp\left[-(W_i{}^0(m_i)+W_j{}^0(m_j)/kT)\right]\}. \quad (74)$$

Here Q is defined as in (18–19–20). The second term in (74) arises because of the interchange degeneracy previously mentioned. If the crystalline field is not cubic, the mean square magnitudes of μ_x, μ_y, μ_z appearing in (74) need not be equal, unlike the case of free atoms considered in Section 4 where there was isotropy except for dipole-dipole forces.

Eq. (73) shows that $A^0=0$, $B^0=\alpha^0$. Consequently the specific heat is by (1), (64–5),

$$c_v=N\frac{d}{dT}\left[d\sum_{m_i}W^0(m_i)\exp\left(-W^0(m_i)/kT\right)\right]+\frac{d}{dT}\left[kT^2\frac{d\alpha^0}{dT}\right]. \quad (75)$$

Here the first term is simply the specific heat of an atom in the crystalline field alone, and arises

from the redistribution of atoms among the various Stark levels as the temperature is varied.[24] The second term is the specific heat due to dipole-dipole interaction between the atoms bound in the crystalline field.

Explicit formulas for α^0 for Fe^{+++} and Gd^{+++} are given in the following paper by Hebb and Purcell, along with graphs of the resulting dipole-dipole specific heat. The latter is, of course, quite different from that obtained with dipole coupling between free atoms, as the interaction is materially modified because the moments tend to be suppressed by the crystalline field as the temperature is lowered. In fact, Hebb and Purcell find that the dipole-dipole specific heat can become negative under certain conditions. This at first seems contrary to one's physical intuition, as one always thinks of a specific heat as necessarily being positive. However, this statement applies only to the total specific heat, i.e., both terms of (75), which is indeed always positive, but there is no reason why a partial specific heat, represented by the second term alone, cannot be negative. The physical reason is that at high temperatures the energy of dipole-dipole interaction is negative. As the temperature is lowered, the susceptibility is at least partially quenched by the crystalline field, and the energy of dipole-dipole interaction hence decreased in absolute magnitude or in other words raised towards zero. Such a rise in energy means a negative specific heat. We have verified that when the crystalline field is removed, (75) reduces to the portion of (35) of comparable approximation (i.e., τ^2), as should of course be the case. We shall omit details of the proof, which is based largely on a method of pairing terms given elsewhere by the author.[25]

Calculation of the susceptibility.—The leading coefficient A^0 in (66) was found to vanish because of (73). However, $A^{(2)}$ does not equal zero, as only the x and y parts of (73) are valid when $H_0 \neq 0$ (i.e., the zero superscripts can be removed only for $q=x, y$). Even use of the x, y portions of (73) is permissible only if the field is applied parallel to one of the principal axes of magnetic susceptibility, which we suppose to be the case.[26] Then

$$\sum_{j>i}(w_{ij})_{\mathrm{Av}} = \sum_{j>i} r_{ij}^{-3}[1+v_{ij}-3\cos^2(z, r_{ij})](\mu_{zi})_{\mathrm{Av}}(\mu_{zj})_{\mathrm{Av}}, \tag{76}$$

with

$$(\mu_{zi})_{\mathrm{Av}} = d_i \sum_{m_i} \mu_{zi}(m_i; m_i) \exp[-W_i(m_i)/kT]. \tag{77}$$

We shall now suppose that if there are several types of atoms, the "inner" or "local" field in a classical calculation is the same for each type of atom, so that we can take

$$\sum_j r_{ij}^{-3}[1+v_{ij}-3\cos^2(z, r_{ij})](\mu_{zj})_{\mathrm{Av}} = (-N\Phi+Nvz')(\mu_z)_{\mathrm{Av}}, \tag{78}$$

where Φ is defined as in (43), and where $(\mu_z)_{\mathrm{Av}}$ is the mean of μ_{zi} over all the different types of atoms, weighted in accordance with their relative abundance. The approximation (78) will be warranted not merely in case the atoms are all alike, but, if we neglect exchange, also in case the paramagnetic neighbors of a given atom are spaced with cubic or spherical symmetry. Then the contributions to (78) will cancel for any sphere taken wholly inside the test body, and there will be a local field only in virtue of the nonspherical shape of the boundary. However, the noncancelling contributions come from regions so far from i that we can neglect the difference in the value of r_{ij}^{-3} contributed by the different species, and (77) is valid. Hence (66) becomes

$$A = -\sum_{j>i}(w_{ij})_{\mathrm{Av}}/kT = -\tfrac{1}{2}k^{-1}T^{-1}N(-N\Phi+Nvz')[(\mu_z)_{\mathrm{Av}}]^2. \tag{79}$$

Now $(\mu_z)_{\mathrm{Av}}$ is the same as the moment M_0/N per atom at infinite magnetic dilution, i.e. the susceptibility in a system composed of atoms devoid of dipole-dipole coupling, but subject to crystalline fields. As already mentioned, the determination of M_0/N is a one-atom problem. By (3), (64), and

[24] If various classes of atoms are present, we must, of course, prorate the first term in (75), also the N-triple product in (65), among the various types.

[25] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 161.

[26] If there are various types of atoms there is the possibility that different classes have different principal axes. Consideration of such an unpleasant complication is, however, not worthwhile until crystalline fields are known much more precisely than at present.

(79) the moment is

$$M=kT\partial \log Z_0/\partial H_0+M_0(\partial M_0/\partial H_0)(\Phi-vz')=M_0+M_0(\partial M_0/\partial H_0)(\Phi-vz'), \tag{80}$$

provided we neglect B in (64), i.e., provided we disregard squares and higher powers of the dipole-dipole interaction. The reader should be careful to distinguish between M and M_0. Namely M is the actual moment, while M_0 is the moment which would result were dipole-dipole and exchange coupling neglected. Now, except for the exchange term v, (80) is exactly the moment which would be obtained by the Lorentz method of the local field, provided we disregard second and higher powers of Φ. Namely in the method of local fields

$$M=M_0(H_0+\Phi M)=M_0(H)+(\partial M_0/\partial H_0)\Phi M_0 \quad \text{to first powers of } \Phi. \tag{81}$$

We thus see that the local field is correct in the first approximation. Our demonstration has been very general, in that we have used quantum mechanics rather than classical theory to describe the interaction of the various dipoles or magnetic moments and have used a perfectly arbitrary atomic model subject to an arbitrary crystalline field. Furthermore, unlike the calculation in Section 4, our proof has included saturation, as it has not been necessary to stop with quadratic terms in H_0 in the expansions (66–67), the complete expressions being used instead.

Second or Gaussian approximation.—When squares of the dipole-dipole interaction are included, the formula for the moment becomes

$$M=\chi_0 H/[1-(\Phi-vz')\chi_0+(Q\chi_0^2-2\alpha^{(2)}\chi_0^{-1}kT)], \tag{82}$$

where $\alpha^{(2)}$, Q are defined as in (72), (18) and $\chi_0=M_0/H$ is the susceptibility at infinite magnetic dilution, i.e., exclusive of dipole-dipole interaction but inclusive of the crystalline field. Here for simplicity we have neglected saturation, and assumed that the atoms are all alike. Eq. (82) is derived from (64–72) in much the same manner as (56) from (46), and the two formulas represent comparable approximations in their respective cases. Thus (82) represents an accuracy comparable with assuming a Gaussian distribution of energies, as explained in Section 5. The portion $2\alpha^{(2)}\chi_0^{-1}kT$ of (82) comes from the last or third term in the formula for B in (68). The first term in this formula does not contribute until fourth powers of the field strength (incipient saturation) are considered. The second term is, as in (51), conveniently handled by adding and subtracting the excluded members; the subtracted part gives rise to $Q\chi_0^2$ in (82). Even without exchange corrections v, (82) is not the same as the formula given by the usual local field theory. The latter has

$$M=\chi_0(H_0+\Phi M), \quad \text{i.e.,} \quad M=\chi_0 H_0/(1-\chi_0\Phi). \tag{83}$$

We have verified that (82) reduces to (56) for free atoms. In general, however, with even the simplest crystalline fields present, the explicit numerical formulas for $\alpha^{(2)}$ prove to be exceedingly cumbersome and laborious to obtain, so that (82) would not be useful even were the Gaussian approximation a good one. An exception to this statement arises if the crystalline potential has cubic symmetry, and the temperature is so low that only the lowest cubic level need be considered. If $2D+1$ be the degeneracy of this level, and if its Zeeman components be $W-W^0=-H_0g'\beta D$, $-H_0g'\beta(D-1)$, $\cdots$, $Hg'\beta D$, then the behavior is mathematically similar to that for free atoms, and so can be handled by the theory of Sections 3–4, provided J be replaced by D and g by g'.[27] This correspondence is established by noting the similarity in the Zeeman patterns and in the elementary magnetic moment matrices.

The above observations enable one to devise a simple approximate interpolation formula for $\alpha^{(2)}$ in (82) in the intermediate temperature region in which the temperature dependence of χ_0 deviates from the simple Curie form because of the crystalline field of dominantly cubic symmetry. Suppose that we have an atom whose angular momentum (spin only in the iron group, total in the rare earths) can be regarded as free at room temperatures, but which at low temperatures has its susceptibility so quenched that only a cubic level of degeneracy $2D+1$ is

[27] We use the notation g' rather than g because with crystalline fields the proportionality factor in the Zeeman formula is no longer necessarily the same as the gyromagnetic ratio g.

inhabited. The considerations of the preceding paragraph and Eq. (56) show that the asymptotic values of $2\alpha^{(2)}kT/\chi_0^3$ for low and high (room temperatures) are, respectively, $-Q(x_D-1)$ and $-Q(x_J-1)$. Here x_J is the value of x obtained by using in (55) the true inner (or in iron group, spin) quantum number J of the atom, while x_D denotes the expression (55) with D substituted for J. Presumably $\alpha^{(2)}/\chi_0^3$ varies monotonically between its limiting values. Moreover, the variation in x is not large; its range is a maximum in the case $D=\frac{1}{2}$, $J=\infty$, where $x_D=3/2$, $x_J=1$ if we neglect exchange. Also the effect of the last term in the denominator of (82) is either subordinate, or else (82) is only a rough approximation because of the poor convergence of the development of the partition function. So not much harm will be done if we use almost any interpolation formula for $\alpha^{(2)}/\chi_0^3$. The simplest is

$$-2\alpha^{(2)}kT/\chi_0^3Q=x_D-1+[(x_J-x_D)(T\chi_0-C_2)/(C_1-C_2)], \quad (84)$$

where C_1 and C_2 are, respectively, the asymptotic values of χ_0T characteristic of high and low temperatures.

Generalized Onsager formula.—Instead of using (82, 84) it is usually more satisfactory to employ a generalization of Onsager's formula obtained by defining ψ as $4\pi\chi_0$ in (58). He derived the result (58) only for free permanent dipoles, where $\chi_0=N\mu^2/3kT=\tau/3T$. That actually his formula can be used for such dipoles even in a crystalline field, provided we take $\psi=4\pi\chi_0$, can be seen from the following argument. Onsager's[21] local field is

$$\mathbf{F}=[3\kappa/(2\kappa+1)]\mathbf{H}_i+\tfrac{1}{3}N[8\pi(\kappa-1)/(2\kappa+1)]\boldsymbol{\mu}, \quad (85)$$

where κ is the permeability $1+4\pi M/H$ and where $\boldsymbol{\mu}$ is the dipole moment vector of the given atom or molecule. The corresponding terms added to the potential function per atom[28] are

$$\Delta V=-[3\kappa/(2\kappa+1)]\boldsymbol{\mu}\cdot\mathbf{H}_i-\tfrac{1}{3}N[4\pi(\kappa-1)/(2\kappa+1)]\boldsymbol{\mu}^2. \quad (86)$$

Now as long as the molecule has a permanent dipole moment, $\boldsymbol{\mu}^2$ will have an invariant constant value μ^2 for all stationary states. This will be the case if only one multiplet component is effective, (Eq. (6)), regardless of how complicated the splitting of this component due to the crystalline Stark field may be. Consequently the second part of (85), which Onsager calls the reaction field (cf. Fig. 1), merely introduces an additive constant term in the energy, and one need retain only the first part of (85) or (86) in dealing with the susceptibility.[29] Then

$$M=\chi_0F=3\kappa\chi_0H/(2\kappa+1). \quad (87)$$

Also by definition

$$\kappa=1+4\pi M/H. \quad (88)$$

Elimination of κ between (87) and (88) shows that (58) applies with $\psi=4\pi\chi_0$.

Specific heat by Onsager's method.—Though the second member of (86) is unimportant for susceptibility if μ^2 is permanent, this portion of (86) persists even when $H=0$ and so gives rise to a field-free specific heat c_v. As kindly pointed out to me by Dr. Hebb, the Onsager procedure is clearly preferable in this respect to that of Lorentz, which furnishes no c_v at all. Now according to classical statistical mechanics the susceptibility χ_0 at infinite magnetic dilution is $N(\boldsymbol{\mu}^2)_{\text{Av}}/3kT$, where the average is a Boltzmann one over the various molecules.[30] It is to be emphasized that this relation, though seldom given is quite general, not being confined to the case of a permanent dipole moment, where the average is clearly unnecessary. (For example, with harmonic oscillators, the mean square amplitude, and hence the average of $\boldsymbol{\mu}^2$, is propor-

[28] The easiest way to establish (86) is to note that the external force acting on a dipole may be written as $\boldsymbol{\mu}\cdot\nabla\mathbf{F}$. The result (86) then follows since force is the negative gradient of the potential and since, except for an unimportant diamagnetic correction, $\boldsymbol{\mu}=\sum e_i[\mathbf{r}_i\times\mathbf{P}_i]/2m_ic$ or (in the electric case) $\boldsymbol{\mu}=\sum e_i\mathbf{r}_i$.

[29] When crystalline fields are present, it is probably a better approximation to replace $\boldsymbol{\mu}^2$ by $3kT\chi_0/N$ in the second member of (86). This change is suggested because in quantum mechanics the square of only the "low frequency" part of the moment makes an important contribution to the susceptibilities, whereas the Onsager model, being classical, gives weight to the square of the entire moment. Since with a crystalline potential χ_0 varies from state to state, the second part of (86), thus modified, can no longer be regarded as an additive constant in computing the susceptibility, and has the effect of displacing the field-free energy levels. At the present state of our knowledge this alteration is of no particular consequence, because the crystalline potential contains enough unknown parameters so that the positions of the energy levels may be considered arbitrary. It does not enter in classical theory inasmuch as with the latter μ^2 and $3kT\chi_0/N$ are identical for permanent dipoles in crystalline fields provided only there is a center of symmetry (cf. Stoner, *Magnetism and Atomic Structure*, p. 176). Thus for permanent dipoles, (91) is the same as (92) at low densities in classical theory even with a crystalline potential, but in quantum mechanics only without the latter. With the potential, (91) is required rather than (92) in quantum theory, because the mode of derivation of (91) implicitly includes the modifications proposed in the present footnote.

[30] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Section 13.

tional to T, and so χ_0 is independent of temperature.) Thus when $H=0$ we have

$$(\Delta V)_{Av}=-kT[4\pi(\kappa-1)/(2\kappa+1)]\chi_0. \quad (89)$$

The corresponding value of the free energy is

$$F=-4\pi NkT\int_0^{\chi_0}[(\kappa-1)/(2\kappa+1)]d\chi_0. \quad (90)$$

The reader is referred to Fowler's *Statistical Mechanics*[31] for a detailed discussion of the rather delicate arguments involved in the derivation of (90) from (89). His presentation is primarily in connection with the Debye-Hückel theory, but can be immediately adapted to our problem. In fact, the Onsager model shows considerable resemblance to the Debye-Hückel one, with of course the difference that the force centers are dipoles rather than ions, and are uniformly rather than statistically distributed in space. In particular, to get (90), the quantity χ_0 can be taken as proportional to Fowler's parameter σ whose growth corresponds to the step-by-step assembly of the system. In (90), κ is then to be regarded as a function of χ_0 obtained by elimination of M between (87) and (88). The specific heat is (cf. Eqs. (1)–(2))

$$c_v=-\frac{d}{dT}\left[T^2\frac{d(F/T)}{dT}\right]$$

$$=4\pi Nk\frac{d}{dT}\left[T^2\frac{(\kappa-1)}{(2\kappa+1)}\frac{d\chi_0}{dT}\right]. \quad (91)$$

At sufficiently high temperatures or low magnetic densities we may replace $(\kappa-1)/(2\kappa+1)$ by $\frac{1}{3}4\pi\chi_0$. In the case of free dipoles, where $\chi_0=N\mu^2/3kT$, Eq. (91) then becomes

$$c_v=16\pi^2N^3\mu^4/27kT^2=Nk(16\pi^2\tau^2/27T^2). \quad (92)$$

This expression is the same as the first term in the formula (35) for c_v obtained by the method of partition functions, provided one uses the value (60) of Q corresponding to a continuum. (In this connection one recalls that μ^2 is the same as $g^2\beta^2J(J+1)$ and that with an arbitrary model the factor 2.8 in (35) is replaced by $\frac{1}{6}Q$ as remarked after Eq. (35)). Thus again there is a gratifying agreement between the Onsager procedure and the exact treatment in the early stages of approximation. This agreement incidentally, is not confined to the case of permanent dipoles, as it can be shown that a general calculation with classical statistics, made by combining the methods of Section 3 and reference 30, yields a formula which is the same as (91) at low densities. For instance, with harmonics oscillators, where $d\chi_0/dT=0$, Eq. (91) yields $c_v=0$, as should be. Eq. (91) ceases to have so exact a basis when quantum mechanics are substituted for classical, but detailed examination of this question shows that any inaccuracy in (91) due to this cause is usually subordinate to the error inherent in the use of any model such as Onsager's. So (91) can be regarded as a convenient formula for c_v. In particular, (91) possesses the satisfactory property of yielding a finite specific heat at $T=0$ even for permanent dipoles, whereas (35) or (92) do not. Also under proper conditions, Eq. (91) can yield a negative dipole-dipole specific heat, which sometimes occurs as mentioned after Eq. (75). If a crystalline field is present, Eq. (91), but not (92), still gives the dipole-dipole contribution to c_v; the first term of (75) must, however, be added to include the part of c_v due to the ordinary action of the field on individual atoms.

It must be cautioned that both for susceptibility and specific heat the initial agreement between the Onsager and kinetic methods is secured only by the rather artificial assumption that the cavity volume equals the mean atomic volume. As a matter of fact, the value (60) of Q is over twice those (20) furnished by actual discrete arrangements. The specific heat formulas are easily, though somewhat arbitrarily, adapted to lower values of Q simply by reducing the expressions (89–92) by a factor $9Q/32\pi^2$. The corresponding patching of the susceptibility formulas is a little more complicated and will be given in a later paper on dielectric constants (after its Eq. (7)).

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[31] R. H. Fowler, *Statistical Mechanics*, second edition, pp. 267–9.

A Theoretical Study of Magnetic Cooling Experiments

M. H. Hebb and E. M. Purcell
Harvard University, Cambridge, Massachusetts

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The experimental results obtained by several investigators on the magnetic cooling method are investigated in the light of (1) the electric crystalline fields acting on the magnetic ions of the paramagnetic salts used in the experiments, and (2) the magnetic dipole-dipole coupling between these ions. These two factors produce anomalous specific heats and departures of the magnetic susceptibility from Curie's law at temperatures below 1°K with which the magnetic method is concerned. Thus the empirical Curie temperature, proportional to the reciprocal of the susceptibility, deviates from the true Kelvin temperature in this region. By the methods developed and discussed in the preceding paper by Van Vleck, numerical calculations of the specific heat and susceptibility have been performed for several salts. The experimental specific heat measured on a Curie scale has been corrected to the Kelvin scale and compared with the calculated results. Fairly good quantitative agreement is obtained, although there is some uncertainty as to the effect of (2) on the susceptibility and hence on the relation between the empirical and Kelvin temperature scales.

Introduction

THE method of adiabatic demagnetization of paramagnetic salts proposed originally by Debye and Giauque[1] has been used by numerous investigators[2–4] to reach temperatures within a few hundredths of a degree of the absolute zero. The purpose of this paper is to consider the theoretical behavior of the substances which have been used and to compare this behavior with the experimental results.

The thermodynamics of the method is well understood. Briefly, the entropy of a sample of a suitable paramagnetic salt as a working substance is lowered isothermally by subjecting the sample to a strong magnetic field while it is kept in thermal contact with a bath of liquid helium. Heat is evolved in this process. Then the working substance is isolated thermally and the magnetic field reduced to zero. Since this change is adiabatic (and reversible), the entropy remains constant and the temperature must fall.

At the temperatures below 1°K with which these experiments are concerned, the Debye specific heat is negligible, and the entropy depends only on the freedom of spatial orientation of the angular momentum (usually due to the spin only) of the paramagnetic ions. Thus if the paramagnetic ions each have an angular momentum $Jh/2\pi$ and this is completely free, there is a $2J+1$-fold degeneracy associated with each ion. The entropy is then constant, and equal to

$$S_0 = R \log (2J+1) \qquad (1)$$

and the specific heat is zero. Here R is the gas constant.

Actually, of course, the ions are never completely free and the entropy deviates from the value (1) at sufficiently low temperatures. The specific heat then has an anomalous value different from zero. These departures occur when kT (k=Boltzmann constant, T=absolute temperature) becomes comparable with the orientation energy of the ion.

The free orientation of the paramagnetic ions is hindered by: 1. the electric fields produced by neighboring nonmagnetic or diamagnetic components of the crystal, and 2. the magnetic and exchange coupling between paramagnetic ions. The former can be treated satisfactorily by the well-known method of crystalline potentials developed by Bethe, Kramers,[5] Van Vleck,[6] and others,[7] and especially by the application of this

[1] P. Debye, Ann. d. Physik **81**, 1154 (1926); W. F. Giauque, J. Am. Chem. Soc. **49**, 1864 (1927).
[2] W. F. Giauque and D. P. MacDougall, Phys. Rev. **43**, 768(L) (1933), J. Am. Chem. Soc. **57**, 1175 (1935); D. P. MacDougall and W. F. Giauque, J. Am. Chem. Soc. **58**, 1032 (1936).
[3] W. J. de Haas, E. C. Wiersma and H. A. Kramers, Physica **1**, 1 (1934); W. J. de Haas and E. C. Wiersma, Physica **2**, 335 and 438 (1935).
[4] N. Kürti and F. Simon, Proc. Roy. Soc. **A149**, 152 and **A152**, 21 (1935).
[5] H. A. Bethe, Ann. d. Physik **3**, 133 (1929); H. A. Kramers, Proc. Acad. Sci. Amsterdam **32**, 1176; **33**, 959 (1929–30).
[6] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford Press), Chap. XI.
[7] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932).

method to S states as given by Van Vleck and Penney.[8] The magnetic interaction will be handled by methods developed by Van Vleck in the preceding paper. We shall neglect the exchange coupling entirely as, with the high magnetic dilution of the salts commonly used in the cooling experiments, the exchange interaction should presumably be subordinate to the true magnetic coupling.

Previous theoretical work

It is to be emphasized that no complete theoretical treatment has so far been accorded this problem. The rôle of the magnetic coupling in reducing the entropy of a paramagnetic salt near the absolute zero has been generally recognized. Little regard, however, has been paid to the influence of this coupling on the magnetic susceptibility used in determining temperatures below 1°K. The importance of electric crystalline fields in their effect on the entropy and susceptibility has also been frequently overlooked, in spite of the fact that in salts of very high magnetic dilution, as, for example, $Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$, the magnetic coupling is very small and consideration of the electric crystalline fields is vital to an interpretation of the behavior.

In their first paper on the demagnetization method, Kürti and Simon[4] made the simplifying assumption that the combined crystalline field and magnetic interaction produced a splitting of the ground state of each ion into $2J+1$ equally spaced component levels, thus completely removing the degeneracy. Their model was admittedly a makeshift, and no justification beyond that of simplicity was given for this form of splitting. It is clear that the problem of the interaction of a collection of magnetic ions is essentially a many ion problem and cannot be reduced in a satisfactory way to a single ion problem, as attempted by Kürti and Simon.

Recently Waller[9] has calculated the anomalous specific heat that arises from the magnetic coupling by a rigorous method similar to that developed independently by Van Vleck.[10] Waller, however, took no account of the influence of crystalline electric fields on the magnetic coupling, so that his formula has only a limited application.

Crystalline Stark splitting

The Stark effect produced by the crystalline fields in the ions which we shall study is of the order of only a cm^{-1} or so, while one usually thinks of a crystalline Stark splitting as being of the order of several hundred or thousand cm^{-1} in magnitude.[5-7] The explanation for this exceedingly small splitting is that, with one exception, all the crystals which have been used in demagnetization experiments contain magnetic ions which are in S states. Now the crystalline field acts only on the orbital part of the angular momentum and is able to influence the spin only through the spin-orbit interaction. Thus, in the usual approximation of Russell-Saunders coupling, S states should show no splitting at all. Actual ions do not conform exactly to Russell-Saunders coupling and Van Vleck and Penney[8] have shown that then a small splitting is produced.

In the cases where the crystal structure of a salt is known, we shall choose a crystalline field of symmetry appropriate to the surroundings of the magnetic ion. For crystals of unknown structure we shall use for simplicity a cubically symmetric field.

Magnetic interaction

The usual static treatment of the magnetic interaction is provided by the method of the Lorentz local field, which takes the field acting on an individual ion as the magnetic field in the crystal augmented by the average field produced by surrounding magnetic ions. This average field is calculated on the assumption that the Lorentz cavity is without influence on the magnetization of the material surrounding the cavity. In other words, the intensity of magnetization outside the cavity is supposed the same as the mean intensity of magnetization of the crystal. The Lorentz local field is thus clearly zero if the crystal is unmagnetized. Hence the Lorentz procedure gives no interaction of the magnetic dipoles in the absence of an external field, unless the temperature is below the Curie point, where

[8] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).
[9] Ivar Waller, Zeits. f. Physik **104**, 132 (1936).
[10] Foregoing paper in this issue, henceforth referred to as L. C.

the crystal acquires a permanent magnetic moment. A refined treatment of the local field which takes proper account of the influence of the cavity and its contents on the surrounding medium has been given recently by Onsager.[11] His method predicts no Curie point and does lead to coupling of the magnetic dipoles even in zero external field.

Van Vleck[10] has developed a new "dynamic" method of calculating the partition function for an assemblage of interacting dipoles, as a power series in the ratio τ/T, where τ is a temperature characterizing the coupling energy of two dipoles and T is the absolute temperature. The entropy and specific heat can be obtained at once from this partition function. Unfortunately, we shall be interested in values of the absolute temperature which are of the order of the characteristic temperature τ. Here, of course, the series expression is very slowly convergent and we shall have either to rely on the static treatment by means of the Onsager local field or content ourselves with the first term of the series in the dynamic method. To a first approximation in τ/T these two procedures are equivalent as regards the specific heat.

Experimental data

The experiments with the demagnetization method which have been so far performed are of two types: 1. essentially mechanical experiments, requiring no calorimetric determinations, and 2. calorimetric measurements. The latter are much the more difficult to perform. In the former, the initial field strength and temperature are measured, then the field is turned off and the final temperature to which the sample falls is determined. If the initial field strength H is sufficiently high, the entropy of the sample depends only on the ratio H/T (T=initial temperature) and can readily be calculated. Since the entropy remains constant during adiabatic demagnetization, this entropy is the same as the field free entropy at the final low temperature. The second type of experiment measures the specific heat as a function of the temperature. This is done by making a single demagnetization to as low a final temperature as possible, and then applying heat to the sample at a known rate, meanwhile observing its temperature change.

As an example of the first class we may cite the measurements of Giauque and MacDougall[2] on $Gd_2(SO_4)_3\cdot 8H_2O$, $Gd(C_6H_4NO_2SO_3)_3\cdot 7H_2O$ and hydrated $Gd(C_{14}H_7SO_5)_3$. The only experimental data of the second class which are available to us are some measurements performed by Kürti and Simon[12] on the specific heats of the alums, $(NH_4)Fe(SO_4)_2\cdot 12H_2O$, $KCr(SO_4)_2\cdot 12H_2O$, and $CsTi(SO_4)_2\cdot 12H_2O$. The results of MacDougall and Giauque on $Gd(C_6H_4NO_2SO_3)_3\cdot 7H_2O$ and hydrated $Gd(C_{14}H_7SO_5)_3$ and of Kürti and Simon on $CsTi(SO_4)_2\cdot 12H_2O$ are particularly interesting because they can be regarded as limiting cases. In these gadolinium compounds the magnetic dilution of the Gd^{+++} ions is so high that one can obtain a satisfactory treatment by disregarding the magnetic coupling entirely and considering only the effects produced by the crystalline field. On the other hand, in the titanium alum, the Ti^{+++} ions are effectively in ^2S states so that here the crystalline field is able to produce no splitting. Thus for $CsTi(SO_4)_2\cdot 12H_2O$ one has to consider only the magnetic coupling and can disregard the crystalline field. It is very satisfying to be able to treat these limiting cases, one with the crystalline field alone and the other with the magnetic coupling alone.

Susceptibility

In the preceding section we made a distinction between those experiments which determined the entropy and those which measured the specific heat. It may be objected that this distinction is an artificial one since the entropy and the specific heat are simply related in terms of the absolute temperature. Unfortunately, however, owing to the difficulty of establishing a true Kelvin scale in the range below 1°K, most observers have used an empirical magnetic or "Curie" temperature scale, defined by extrapolation of Curie's law for the magnetic susceptibility. Thus the determinations of entropy and specific heat discussed above are referred to a reciprocal susceptibility scale and not to the Kelvin tem-

[11] Lars Onsager, J. Am. Chem. Soc. **58**, 1486 (1936). See also L. C., Sections 5 and 6 and especially Fig. 1.

[12] Only the data on the ferric alum have been published (reference 4). We are greatly indebted to Dr. Kürti for communicating the results on the chromic and titanium alums to us in advance of publication.

perature scale. Now, by the very nature of the method, the temperatures obtained will be in the region where Curie's law breaks down, *viz.*, where kT is comparable with the crystalline Stark splitting or the magnetic interaction energy. Hence the temperatures and specific heats found experimentally using the magnetic scale may differ appreciably from the thermodynamic temperatures and specific heats. It is thus necessary, in interpreting the experiments, to calculate the magnetic susceptibility.

Following Kürti and Simon,[4] let us designate temperatures measured on the Curie scale by an asterisk, as T^*. Then $T^*=C/\chi'$ where χ' is the magnetic susceptibility and C is the constant which appears in Curie's law, $\chi'=C/T$ at higher temperatures where this law is valid. When kT becomes comparable with the magnitude of the crystalline splitting, the Stark levels of the ion will no longer be equally populated, and in general the effective moments of the magnetic ions will be reduced as compared to the moments of free ions. This tends to lower the susceptibility below the value given by Curie's law, or in other words, to make T^* greater than T. We must also consider the influence of the magnetic coupling of the ions on the susceptibility. There are three approximate ways of representing this interaction, *viz.*, the method of the Lorentz local field, the Onsager[11] modification of the Lorentz method and the Gaussian formula derived by Van Vleck.[13] In discussing the different results to be expected when these various methods are used, it may be well to confine our attention temporarily to the case of a long rod-like sample, for which the effect of the "demagnetizing" field due to the surface polarization of the magnetized sample may be neglected.[14] The demagnetizing factor, D, will be discussed later; its effect is to *increase* T^* by a definite amount which depends on the density of magnetic ions in the sample, and upon the shape of the sample, but which is independent of the temperature. The demagnetizing factor vanishes for an infinitely long rod, and the susceptibility as calculated by the method of the Lorentz local field is always increased by the magnetic coupling. In fact, there is a Curie point[15] below which there is spontaneous magnetization, i.e., the susceptibility becomes infinite. Thus, with the Lorentz hypothesis, T^* becomes zero at the Curie point. Neither the Onsager nor the Gaussian formula shows a Curie point. Onsager's treatment does increase the susceptibility over the value given by Curie's law, but only by a small factor ranging from 1 to 1.5. In cases of high magnetic dilution this factor may be offset by a decrease in susceptibility due to the crystalline Stark splitting. It seems probable that the most accurate representation of the susceptibility at low temperatures is that afforded by the method of Onsager.

Some idea of the deviation of T^* from T as the temperature is lowered can be obtained as follows: Let us expand the ratio T^*/T as a power series in $1/T$. Then

$$T^*=T(1-A/T+B/T^2\cdots).$$

Now it has been shown[7] that for a crystal powder there is no contribution to the coefficient A from the crystalline splitting. Thus A comes entirely from the magnetic coupling and is always positive, as can readily be proved.[16] On the other hand, both crystalline splitting and magnetic coupling[16] can enter into B. Both contributions are in general positive for a crystal powder. Thus as T is lowered from very high values, where T^* is sensibly the same as T, T^* first becomes less than T, i.e., the departure of the susceptibility from the value given by Curie's law is in the ferromagnetic direction. At still lower temperatures the term in $1/T^2$ becomes important and tends to raise T^* above T. Only if B is sufficiently large in comparison with A^2, i.e., if the crystalline splitting is sufficiently large compared to the magnetic coupling, will T^* actually exceed T in the range of the experiment.

[13] L. C., Sections 4 and 5.

[14] We should like to emphasize the fact that, where feasible, the use in cooling experiments of samples in ellipsoidal shapes, for which the demagnetizing factor can be calculated, greatly facilitates the theoretical interpretation of the results. The special forms of the sphere and the very prolate ellipsoid naturally suggest themselves. The latter is sufficiently well approximated by a thin rod since D for such an ellipsoid is small anyway.

[15] The possibility of a Curie point due to dipole-dipole coupling was suggested by P. Debye, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math.-Phys. Klasse. **86**, 105 (1934).

[16] For a cubic lattice of magnetic ions or for a classical continuous magnetic distribution, $A=(4\pi/3-D)\tau/3$ where D is the demagnetizing coefficient and τ is defined by Eq. (7). If one neglects the crystalline splitting, one finds the values $B=0$ (Lorentz), $B=2(4\pi\tau/9)^2$ (Onsager—continuous magnetic distribution), $B=Q\tau^2[1+\frac{3}{8}J(J+1)]/9$ (Gaussian) with Q as defined in L. C.

I. Salts for which Only Crystalline Splitting Need Be Considered

Gadolinium nitrobenzene sulfonate heptahydrate —$Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$

As pointed out in the introduction this is a salt of extremely high magnetic dilution, and we shall calculate its entropy considering only the crystalline splitting and neglecting contributions from the spin-spin coupling of the ions. The crystal structure of the salt is unknown, but it is reasonable to assume in a first attack that the surroundings of the gadolinium ions have cubic symmetry. The matrix elements of a cubic potential have been given by Penney and Schlapp[7] for the usual J, M representation. Using the analysis of Van Vleck and Penney,[8] one readily finds that the cubic field splits the 8-fold degenerate ^8S ground state of Gd^{+++} into two doubly degenerate levels and one quadruply degenerate level. The latter lies between the two former and the spacings are in the ratio 3 : 5. Thus the partition function for the ion is either[17]

$$Z_c = 2(1+2e^{-3\delta/8kT}+e^{-\delta/kT}) \qquad (2)$$

or

$$Z_c' = 2(1+2e^{-5\delta/8kT}+e^{-\delta/kT}) \qquad (2a)$$

with δ equal to the over-all energy separation. It is not possible to predict which of (2) and (2a) is actually realized. We have found slightly better agreement with the first choice, and henceforth we shall assume the splitting is that represented by Eq. (2).

The entropy S per gram-ion in zero magnetic field is at once found from (2) by the formula

$$S = R\partial(T \log Z)/\partial T. \qquad (3)$$

This calculated entropy for $\delta = 1.4$ deg. $= 0.98$ cm^{-1} is shown by the full line in Fig. 1. The splitting δ has been adjusted to obtain agreement with MacDougall and Giauque's[2] experimental results. The open circles in Fig. 1 represent the entropy calculated from their data on initial magnetic field and temperature prior to demagnetization, and plotted against the final empirical magnetic temperature T^*. The dots represent the same data, but with a calculated correction applied to reduce the temperature to the Kelvin scale.

[17] Cf. R. H. Fowler, *Statistical Mechanics*, second edition (Cambridge), p. 839ff, where (2a) is used instead of (2).

In deducing the ordinates of the circles and dots in Fig. 1, we have supposed that effects of crystalline splitting on the entropy can be neglected in the initial field. Clearly, this will be allowable if the splitting of the ground state of the magnetic ion by the magnetic field is considerably larger than the splitting produced by the crystalline field, i.e., if $gJ\beta H \gg \delta$ ($g=2$, $J=7/2$, $\beta=$Bohr magneton). Then the entropy in the magnetic field is given by Eq. (3) with

$$Z(H, T) = \sum_{M=-7/2}^{7/2} \exp(-2M\beta H/kT). \qquad (4)$$

Actually, for the highest point shown in Fig. 1, $7\beta H/\delta \approx 1$ so that here the entropy calculated with (4) will be slightly too high. Giauque and MacDougall attempted to take this into account essentially by lowering all points by the difference between $S_0 = R \log 8$ and the actual field free entropy at the initial temperature. It is clear that their procedure[18] is correct only when the magnetic field is small and that our method which neglects the crystalline splitting is better at high field strengths.

In applying Eq. (4), we have made the usual Lorentz and demagnetization[19] corrections for the fact that the local field H_{loc} acting on the individual ions differs from the field H_0 before introduction of the sample. Thus, we have replaced the H which appears in Eq. (4) by $H_{\text{loc}} = H_0 + (4\pi/3 - D)M$ where M is the intensity of magnetization of the sample, and D is the demagnetizing coefficient. We have taken $D = 0.38$ for the cylindrical sample used by MacDougall and Giauque[2] (length 12 cm, diameter 1.6 cm). Only a rough calculation of M

[18] Giauque and MacDougall's method may be indicated as follows: Let $S_0 = R \log 8$ be the entropy per half-mole of free ions at the initial temperature T_i, in zero magnetic field. Let S_0' be the entropy of these ions in field H at the same temperature. Let S and S' be the entropies at $H=0$ and $H=H$, respectively, at the same temperature, of one half-mole of ions in the actual crystal. We wish to determine S'. Giauque and MacDougall now assume that $(S_0 - S_0') = (S - S')$. Clearly this is permissible only if $(S_0 - S)$ and $(S_0 - S_0')$ are both small. For example, $S_0 - S_0'$ approaches $R \log 8$ for high fields and, if $S_0 - S$ is appreciable, $(S_0 - S) + (S_0 - S_0')$ may exceed $R \log 8$ and hence cannot equal $(S_0 - S')$. In general, to calculate S', we must use the accurate partition function including both Stark and Zeeman splitting; but if the Zeeman splitting is much greater than the Stark splitting, as will be the case when H is large, it will be a good approximation to neglect the latter entirely, and to calculate S' from (4).

[19] E. C. Stoner, *Magnetism and Matter* (Methuen), p. 38.

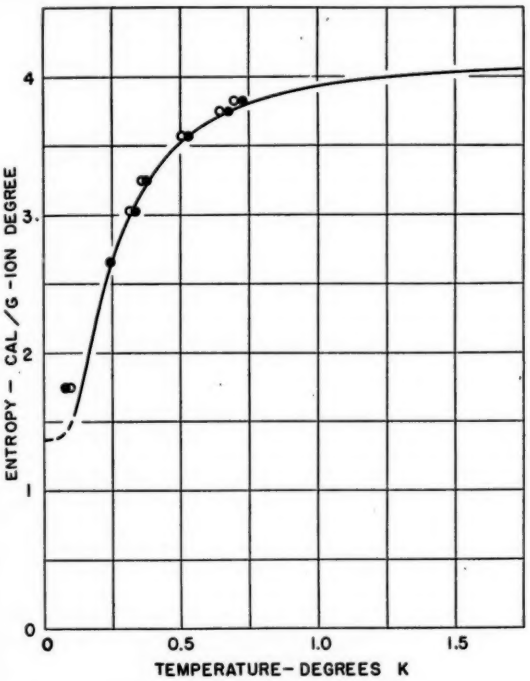


FIG. 1. Entropy of gadolinium nitrobenzene sulfonate heptahydrate. The curve is calculated for a splitting $\delta=1.4°=0.98$ cm^{-1} with neglect of dipole-dipole coupling. The entropy derived from MacDougall and Giauque's magnetic measurements is shown by circles on the empirical T^* scale and by dots after correction to the T scale with the Lorentz hypothesis.

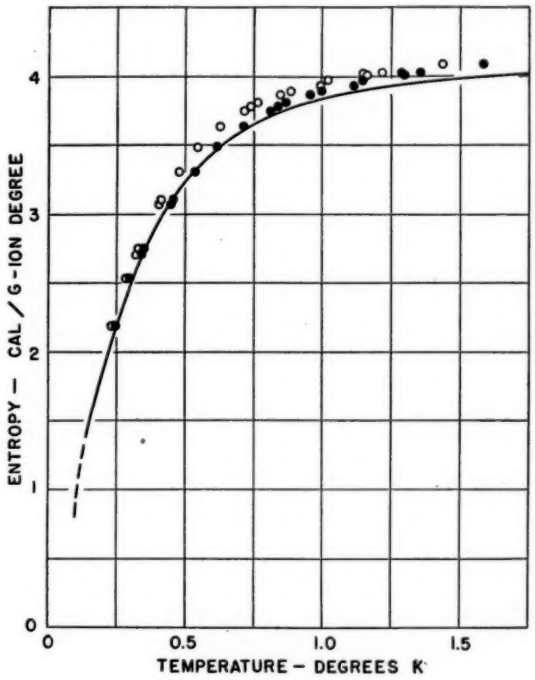


FIG. 2. Entropy of gadolinium sulfate octahydrate. The curve is calculated for a splitting $\delta=1.4°=0.98$ cm^{-1} and includes the dipole-dipole entropy. The entropy derived from Giauque and MacDougall's magnetic measurements is represented by the circles on the empirical T^* scale and by the dots after correction to the T scale with Onsager's hypothesis.

(on the assumption of a density of 2g/cc) could be made as the true density of the salt was unknown to us. However this is not serious as the correction is quite small owing to the great magnetic dilution of the gadolinium ions.

The reduction of the Curie temperature readings to the Kelvin scale requires a knowledge of the magnetic susceptibility for gadolinium ions in a cubic crystalline field. The magnetic moment matrix for Gd^{+++} in a cubic representation is found to be

$$\mu=2\beta\left\|\begin{array}{cccc|c} 7/6 & 0 & -\tfrac{1}{3}\sqrt{35} & 0 & 0 \\ 0 & 1/2 & 0 & -\sqrt{3} & 3\delta/5 \\ -\tfrac{1}{3}\sqrt{35} & 0 & 11/6 & 0 & 3\delta/5 \\ 0 & -\sqrt{3} & 0 & -3/2 & \delta \end{array}\right\| \quad (5)$$

together with a similar matrix with all signs reversed. The rows and columns are labeled according to the energy. Using standard methods,[6, 7] we find from (5) that the volume susceptibility is

$$\chi_0=\gamma\tau/3T \quad (6)$$

with

$$\tau=Ng^2\beta^2J(J+1)/k \quad (7)$$

and

$$\gamma=2Z_c^{-1}\left\{\left(\frac{7}{27}+\frac{320}{81}\frac{kT}{\delta}\right)+\left(\frac{130}{189}-\frac{6016}{2835}\frac{kT}{\delta}\right)e^{-3\delta/8kT}+\left(\frac{3}{7}-\frac{64}{35}\frac{kT}{\delta}\right)e^{-\delta/kT}\right\}. \quad (8)$$

Here N is the number of magnetic ions per cc; in our case $N\backsimeq 1.3\times10^{21}$ and $\tau\backsimeq 0.05$ deg. The function γ is so chosen that $\gamma\to1$ at high temperatures or vanishingly small splitting. We use χ_0 to indicate the susceptibility exclusive of magnetic coupling, i.e., $L\chi_0/N$ is the molar susceptibility at infinite dilution. We shall reserve χ for the ratio of the intensity of magnetization

to the actual field H in the sample. The susceptibility measured experimentally we shall call χ'. This is the ratio of the intensity of magnetization to the magnetic field H_0 before introduction of the sample. These three susceptibilities are related as follows:

$$\chi=\chi_0/(1-4\pi\chi_0/3) \quad \text{(Lorentz)}, \tag{9}$$

$$\chi=\chi_0\left\{\frac{3}{4}-\frac{3}{16\pi\chi_0}+\left(\frac{9}{16}+\frac{3}{32\pi\chi_0}+\frac{9}{256\pi^2\chi_0^2}\right)^{\frac{1}{2}}\right\} \quad \text{(Onsager)}, \tag{10}$$

$$\chi'=\chi/(1+D\chi), \tag{11}$$

where D is the demagnetizing coefficient. For $Gd(C_6H_4NO_2SO_3)_3\cdot 7H_2O$, the characteristic temperature τ is small so that there is no appreciable difference between (9) and (10) at the temperatures with which we have to deal. Now,

$$T^*=\tau/3\chi'=\tau/3\chi+D\tau/3, \tag{12}$$

the second equality following from Eq. (11). Hence, using (9) we find

$$T^*=T/\gamma-(4\pi/3-D)\tau/3.$$

This is the final equation by which the horizontal shift between the circles and dots in Fig. 1 has been obtained. As stated previously, $\tau=0.05°$, $D=0.38$ and γ is given by Eq. (8).

It is not believed that the deviation of the lowest point from the curve is significant. Neither inclusion of the spin-spin entropy in the calculated curve nor the more refined Onsager treatment of the susceptibility can move the point nearer the curve. The discrepancy as shown comes from the great reduction in the susceptibility at this low temperature due to the crystalline field. With the inverted splitting pattern, corresponding to (2a) instead of (2), this diminution is not so great and it is quite possible that a more elaborate calculation using fields of lower symmetry would allow the temperature correction here to be in the ferromagnetic direction as it is at higher points, thus bringing the lowest point closer to the curve.

We shall return to a consideration of another gadolinium salt ($Gd_2(SO_4)_3\cdot 8H_2O$) in a later section where we calculate the spin-spin contribution to the entropy. The crystalline potential part of the problem is the same as that given here.

II. Salts for which Only Magnetic Coupling Need Be Considered

Cesium titanium alum—$CsTi(SO_4)_2\cdot 12H_2O$.

This is the other extreme case, *viz.*, a salt in which the crystalline splitting can be disregarded and in which only spin-spin effects need be considered. We have already stated that this procedure is possible because the Ti^{+++} ion[6] is effectively in a ^2S state whose double degeneracy no crystalline field is able to lift. (A free titanium ion would be in a ^2F state, but the crystalline field quenches the orbital angular momentum.)

We shall here be interested in the specific heat rather than the entropy as the most extensive experiments on this salt are Kürti and Simon's measurements[12] on its specific heat.

The spin-spin specific heat to be expected when no crystalline splitting exists has been given as a power series in τ/T by Waller,[9] who, however, evaluated only the first nonvanishing term, that in $(\tau/T)^2$. Van Vleck (L. C.) has independently deduced the first three terms. The coefficients in the series depend on the moments of the magnetic ions in the crystal and upon the distribution of ions in the lattice. We shall not give the general formulas but shall immediately specialize to the face-centered arrangement for the alums, and to $J=S=\frac{1}{2}$. Van Vleck's formula for the specific heat is then

$$C_v=R\{2.40(\tau/T)^2-4.35(\tau/T)^3-13.5(\tau/T)^4\cdots\} \tag{13}$$

with τ as given by Eq. (7). The numerical values of the quantities entering into τ are $N=L/290$ per cc, $g=2$, $J=S=\frac{1}{2}$. Substituting, we find $\tau=0.0038$ deg.

An alternative expression for the spin-spin specific heat is provided by considering the coupling between the magnetic ions and Onsager's reaction field.[20] This leads to the formula

$$C_v=-R\tau(4\pi/3)^2\frac{d}{dT}\{\chi[1+8\pi\chi/3]^{-1}\}, \tag{14}$$

where χ is given by Eqs. (10) and (6) with $\gamma=1$.

[20] L. C., Section 6, especially Eq. (91).

The graph of Eq. (13) is shown in Figs. 3 and 4. The two curves marked A are the same and are drawn using only the first term of Eq. (13). The dotted curve B in Fig. 3 includes all three terms given in Eq. (13). The specific heat calculated with Eq. (14) is represented by C of Fig. 4. The remaining graphs in Figs. 3 and 4 show the experimental data both uncorrected (C, Fig. 3) and corrected according to the three procedures —Lorentz (D, Fig. 3), Onsager (B, Fig. 4) and Gaussian (E, Fig. 3)—for the difference between T^* and T and the deviation of dT^*/dT from unity, i.e., for the departure of the susceptibility from Curie's law. We now turn to a discussion of these corrections.

Since there is no crystalline splitting, the susceptibility χ_0 exclusive of coupling and demagnetization obeys Curie's law and has the value obtained from Eq. (6) with γ replaced by unity. Formulas (9) and (10) give the connection between χ and χ_0 according to Lorentz and Onsager, respectively. A third way of making this connection is provided by the Gaussian formula

$$\chi=\chi_0\{1-4\pi\chi_0/3+12\eta\chi_0^2\}^{-1}. \qquad (15)$$

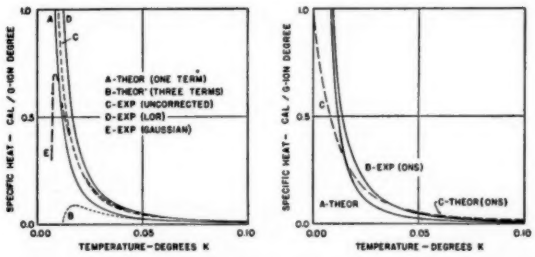
Here η is a function[21] of the lattice spacing and the moments of the magnetic ions which never differs greatly from unity. In our case $\eta=1.20$ $\times(3/2)=1.80$.

The three Eqs. (9), (10) and (15) together with (6) and (12) at once yield the relations between T^* and T, according to the three procedures. For the demagnetizing coefficient which appears in (12), we have taken $D=1.7$. This value is obtained by approximating Kürti's cylindrical sample (length/diameter$=2.5$) by an ellipsoid.[19]

In reducing the observed curve C, Fig. 3, to the Kelvin scale it is necessary to remember that the quantity actually measured is not the true specific heat C_v but is rather $C_v^*=C_v(dT/dT^*)$. Hence both ordinates and abscissas of points on curve C must be adjusted.

It is rather remarkable that the first term of Eq. (13) represents the general trend of the experimental curves as well as it does. It will be noticed that the first term (curves A) fits the

[21] L. C. Eqs. (56) and (82).



FIGS. 3 AND 4. Specific heat of cesium titanium alum. To Kürti and Simon's calorimetric measurements, shown by the curve labeled EXP (UNCORRECTED), corrections have been applied to take into account the difference between the apparent temperature T^* as recorded on a Curie scale and the true thermodynamic temperature T. These corrections cannot be made precisely and have different values according as the Lorentz, Gaussian, or Onsager formula is employed for the susceptibility.

data better and corresponds more closely to the Onsager specific heat (curve C, Fig. 4) than does B of Fig. 3, which includes three terms of Eq. (13). This fact is comforting, since, in later sections where splitting cannot be disregarded, it is not feasible to evaluate terms beyond the first.

There is not a great difference between the Lorentz and Onsager corrections to the susceptibility, although the curves lead to a slight preference for Onsager's method. However, both of these corrections seem better than the Gaussian one. The latter predicts a maximum in the susceptibility or a minimum in T^* (where curve E, Fig. 3, would cross the axis) and although this minimum was not attained in Kürti's experiments on titanium alum, magnetic temperatures below the predicted minimum have been reached with other salts.

It is to be noted that the calculations have involved no adjustable parameter such as the splitting. Hence the test of the various methods of handling the susceptibility is perhaps more significant here than in later salts where such a parameter must be introduced.

III. Salts for which Both Crystalline Splitting and Magnetic Coupling Must Be Considered

Gadolinium sulfate octahydrate—$Gd_2(SO_4)_3\cdot 8H_2O$

The individual gadolinium ions are much closer together in the hydrated sulfate than in the hydrated nitrobenzene sulfonate and the

spin-spin interaction is correspondingly greater. We shall suppose again that the gadolinium ions are situated in a cubic crystalline field. Then the crystalline splitting part of the problem is the same for the hydrated sulfate as for the nitrobenzene sulfonate.

Now, the partition function for one gram-ion (L ions) including the spin-spin coupling is

$$Z^L = Z_c{}^L(1+\Omega\tau^2/T^2\cdots)^L \qquad (16)$$

with the partition function Z_c for a single ion in the cubic field given by (2). Here τ is found from Eq. (7) with $N=L/124$ per cc, $g=2$ and $J=S=7/2$ to be $\tau=0.189$ deg. We shall not give the general form of Ω appearing in (16) as this may be obtained from Van Vleck's paper.[22] It depends on the lattice arrangement, crystalline splitting, temperature and on the magnetic moment elements of the ion in the cubic field. With the help of (5), we find that for gadolinium sulfate

$$\begin{aligned}\Omega = 1.49\times 4Z_c{}^{-2}\Big\{&\left(\frac{49}{729}+\frac{2560}{729}\frac{kT}{\delta}\right)\\ &+\left(\frac{1060}{729}+\frac{5696}{945}\frac{kT}{\delta}\right)e^{-3\delta/8kT}\\ &+\left(\frac{16900}{35721}+\frac{520192}{178605}\frac{kT}{\delta}\right)e^{-3\delta/4kT}\\ &+\left(\frac{2}{9}-\frac{4096}{945}\frac{kT}{\delta}\right)e^{-\delta/kT}\\ &+\left(\frac{548}{441}-\frac{5696}{945}\frac{kT}{\delta}\right)e^{-11\delta/8kT}\\ &+\left(\frac{9}{49}-\frac{512}{245}\frac{kT}{\delta}\right)e^{-2\delta/kT}\Big\}. \qquad (17)\end{aligned}$$

When (16) is inserted into (3), one finds that the second factor of (16) yields an additive spin-spin entropy which is

$$S_s = R\tau^2\frac{d}{dT}\left(\frac{\Omega}{T}\right). \qquad (18)$$

The part arising from the first factor of (16) is the same as the crystalline splitting entropy obtained previously.

[22] L. C. Eq. (74). The quantity α^0 is the same as $N\Omega\tau^2/T^2$ in our notation.

In Fig. 2 we have shown the entropy curve calculated by means of Eqs. (2), (3), (17) and (18), with the same value ($\delta=1.4$ deg. $=0.98$ cm^{-1}) of the splitting as was found previously for the nitrobenzene sulfonate. The experimental data are represented by the circles and dots according to the same scheme used in connection with Fig. 1, except that the Onsager Eq. (10) has been used instead of the Lorentz Eq. (9) in reducing the magnetic temperature T^* to the Kelvin temperature T.

It will be seen that the dots in Fig. 2 lie systematically above the calculated curve for temperatures higher than 0.7°K. This is due to our neglect of crystalline splitting in calculating the reduction in entropy by the magnetic field at the initial temperature. As explained in connection with Fig. 1, this neglect results in too high an entropy when the initial magnetizing field is small.

It is very gratifying that the same splitting can be used in both gadolinium sulfate and nitrobenzene sulfonate and that the difference in their behavior can be attributed entirely to the change in magnetic interaction attending magnetic dilution. One might not expect, *a priori*, to find the same crystalline fields acting on the gadolinium ions in two such different compounds. However, the result is not unreasonable, since the groups closest to the gadolinium ions are probably water molecules and their arrangement may be nearly alike in the two salts.

Ammonium ferric alum—$NH_4Fe(SO_4)_2\cdot 12H_2O$

It is known that the trivalent ion in an alum is surrounded by six water molecules forming a regular octahedron. Hence the crystalline field acting on the Fe^{+++} ion should be closely cubic. The form of the Stark splitting produced in the ^6S ground state of Fe^{+++} by a cubic crystalline field has been given by Van Vleck and Penney.[8] They find that the six levels of the ^6S state separate into two, one doubly and the other quadruply degenerate. We have supposed that the former state lies below the latter. Then the partition function for a single ion in the crystalline field is

$$Z_c = 2(1+2e^{-\delta/kT}), \qquad (19)$$

where δ is the over-all splitting. The complete

partition function per gram-ion, including magnetic coupling, is again given by Eq. (16). For the ferric alum $N=L/276$ per cc, $g=2$, $J=S=5/2$ and by (7) $\tau=0.0472$ deg.

We require the magnetic moment matrix to evaluate the function Ω which occurs in (16) and to calculate the susceptibility. This can be obtained from Van Vleck and Penney's Eq. (5) by diagonalizing the cubic terms and then picking out the coefficients of the field strength H. The result is

$$\mu=2\beta\begin{Vmatrix} 5/6 & 0 & \frac{2}{3}\sqrt{5} \\ 0 & -1/2 & 0 \\ \frac{2}{3}\sqrt{5} & 0 & -11/6 \end{Vmatrix}\begin{matrix}0\\ \delta\\ \delta\end{matrix} \qquad (20)$$

together with the same matrix having all signs reversed. From (20) one finds

$$\Omega=1.20\times 4Z_c^{-2}\left\{\left(\frac{25}{441}+\frac{64}{49}\frac{kT}{\delta}\right)+\left(\frac{772}{441}+\frac{64}{21}\frac{kT}{\delta}\right)e^{-\delta/kT}+\left(\frac{676}{441}-\frac{640}{147}\frac{kT}{\delta}\right)e^{-2\delta/kT}\right\}. \qquad (21)$$

The specific heat corresponding to the partition function (16) is readily shown to be

$$C_v=R\frac{d}{dT}T^2\frac{d}{dT}\log Z_c+R\tau^2T\frac{d^2}{dT^2}\left(\frac{\Omega}{T}\right). \qquad (22)$$

The first term arises from the crystalline splitting and the second from the magnetic coupling.

The susceptibility χ_0 exclusive of magnetic coupling satisfies Eq. (6) with

$$\gamma=2(21Z_c)^{-1}\{(5+32kT/\delta)+(26-32kT/\delta)e^{-\delta/kT}\}. \qquad (23)$$

In Fig. 5 (curve A) we have shown the specific heat calculated with help of Eqs. (19), (21) and (22) for a splitting of $\delta=0.225$ deg. $=0.157$ cm^{-1}. The first term of (22) which represents the part due to the crystalline splitting is indicated by the dashed curve D. The uncorrected experimental specific heat measured by Kürti and Simon[4] is shown at C. We have obtained curve B by adjusting the temperature scale with the Lorentz formula for the susceptibility, i.e., by Eqs. (6), (9), (12) and (23) with $D=1.4$.

We have been unable to obtain satisfactory agreement between the calculated curve A and the experimental curve adjusted by the Onsager method. We believe that the trouble is probably not in the treatment of the susceptibility by the Onsager procedure but in the inaccuracy in representing the expansion (16) by its first term. It should be noticed that, at a given temperature, the spin-spin specific heat is more important in the ferric alum than in the titanium alum because of the difference in spin. Hence any discrepancies due to our approximate handling of this part of the specific heat will be more glaring.

The treatment by the Gaussian formula is even worse than the Onsager method. Here the Gaussian formula is evidently at fault since it predicts a minimum magnetic temperature of $T^*=0.071°$, which is considerably above the lowest experimental values of T^* shown in Fig. 5.

It is also possible that more satisfactory results could be obtained by inverting the pattern of Stark levels, so that the quadruply degenerate level would lie below the doubly degenerate level. We found it necessary to make the other choice in order to get approximate agreement with the early experimental data on ammonium ferric alum. However, we have been informed of some very recent experiments of Simon[23] which tend to confirm our suspicion that the quadruply degenerate level is actually on the bottom. Simon has found that $NH_4Fe(SO_4)_2\cdot 12H_2O$ becomes definitely ferromagnetic at $T=0.034°$K, this temperature being measured on a true thermodynamic scale established by a method suggested by Debye and others.[24] Now in our theory an *upper limit* to the theoretical Curie point temperature, T_c, is clearly given by using the Lorentz local field formula for an infinitely long sample. This predicts a Curie point, $T_c=0.029°$K if we take the double level on the bottom. (No additional assumptions or parameters are involved here.) Due to the large moment associated with two of the components of the quadruply degenerate level, the corresponding theoretical

[23] Private communication from Professor F. Simon to Professor P. W. Bridgman. Cf. also N. Kürti, P. Lainé and F. Simon, Comptes rendus **204**, 675 (1937).

[24] P. Debye, Physik. Zeits. **35**, 923 (1934); W. H. Keesom, J. de phys. et rad. **5**, 373 (1934).

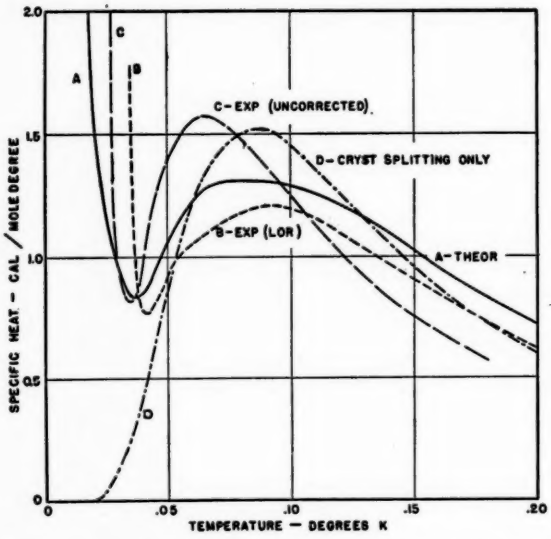


FIG. 5. Specific heat of ammonium ferric alum for a splitting $\delta = 0.225° = 0.157$ cm^{-1}.

T_c may be raised to nearly 0.05°K, or well above the experimental value, if one takes the levels inverted. We have also compared our results with a preliminary determination of two points on the T^* *vs.* T curve, reported by Kürti and Simon.[4] Here again the poor agreement suggests that some change is needed.

In repeating the calculations with the scheme of levels inverted, one would doubtless need to introduce a small field of lower than cubic symmetry in order to split the lower state into two doubly degenerate levels. This would involve an additional parameter, increasing both the arbitrariness and the laboriousness of the calculations. We have not felt that such calculations are advisable until we have more experimental data with which to compare our results.

Potassium chromic alum—$KCr(SO_4)_2 \cdot 12H_2O$

The ground state of the free Cr^{+++} ion is a ^4F but the susceptibilities of chromic salts conform closely to the Bose-Stoner value,[6] showing that the orbital angular momentum is quenched by the crystalline field leaving the spin free. The lowest state of the chromic ion in the cubic field[7] belongs to the fourfold representation Γ_8 of the cubic group (Bethe's[5] terminology). Thus a field of purely cubic symmetry leaves a fourfold degeneracy in the ground state.

Examination of the crystal structure of the alums[25] shows that the octahedron formed by the six water molecules about the trivalent ion is not symmetrically oriented with respect to the cubic axes of the crystal. One sees that there is a preferred trigonal axis which coincides with one of the body diagonals of the cubic crystal lattice. As already mentioned, the trivalent ions in an

TABLE I. *Predicted relation between Kelvin and Curie temperature scales. The table shows values of* $\Delta = 100(T^* - T)/T$, *computed by using the relation* $T^* = C/\chi'$. *The subscript Lor or Ons indicates that* χ' *has been calculated by the Lorentz or Onsager formula for the susceptibility. This table applies directly only to very long samples* ($D = 0$). *For ellipsoids of finite length, one must add* $D_T/3$ *to the values of* T^* *obtained from the table.*

$Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$ $\quad \tau = 0.05°$, $\delta = 1.4° = 0.98$ cm^{-1}

T°K	Δ_{Lor}	T°K	Δ_{Lor}	T°K	Δ_{Lor}
1.75	−3.1%	0.80	−5.2%	0.20	+0.5%
1.50	−3.7	.60	−5.8	.10	+15
1.25	−4.1	.40	−6.0	.05	+4.0
1.00	−4.6	.30	−4.7	.023	−100

$Gd_2(SO_4)_3 \cdot 8H_2O$ $\quad \tau = 0.189°$, $\delta = 1.4° = 0.98$ cm^{-1}

T°K	Δ_{Ons}	T°K	Δ_{Ons}	T°K	Δ_{Ons}
1.75	−10.2%	0.80	−15.0%	0.20	0.0%
1.50	−11.5	.60	−15.6	.10	34
1.25	−12.7	.40	−14.5	.05	75
1.00	−14.0	.30	−11.0	.00	157

$CsTi(SO_4)_2 \cdot 12H_2O$ $\quad \tau = 0.0038_5°$

T°K	Δ_{Lor}	Δ_{Ons}	T°K	Δ_{Lor}	Δ_{Ons}
0.10	−5.4%	−4.8%	0.03	−18%	−12.7%
.08	−6.8	−5.9	.02	−27	−16.5
.06	−9.0	−7.5	.01	−54	−23
.05	−10.8	−8.8	(.0054	−100%)	
.04	−13.5	−10.2	.00		−33

$NH_4Fe(SO_4)_2 \cdot 12H_2O$ $\quad \tau = 0.0472°$, $\delta = 0.225° = 0.157$ cm^{-1}

T°K	Δ_{Lor}	T°K	Δ_{Lor}	T°K	Δ_{Lor}
0.15	−33%	0.08	−47%	0.04	−70%
.12	−38	.06	−52	.03	−95
.10	−42	.05	−58	.0285	−100

$KCr(SO_4)_2 \cdot 12H_2O$ $\quad \tau = 0.0204°$ $\quad \delta = 0.20° = 0.14$ cm^{-1} (Lorentz) $\quad \delta = 0.17° = 0.12$ cm^{-1} (Onsager)

T°K	Δ_{Lor}	Δ_{Ons}	T°K	Δ_{Lor}	Δ_{Ons}
0.15	−14%	−9.6%	0.04	−40%	−2.0%
.12	−16	−9.8	.03	−57	+1.5
.10	−18	−9.5	.02	−96	5.5
.08	−21	−8.8	.01		9.0
.06	−26	−6.5	.00		11.0

[25] H. Lipson and C. A. Beevers, Proc. Roy. Soc. A148, 664 (1935).

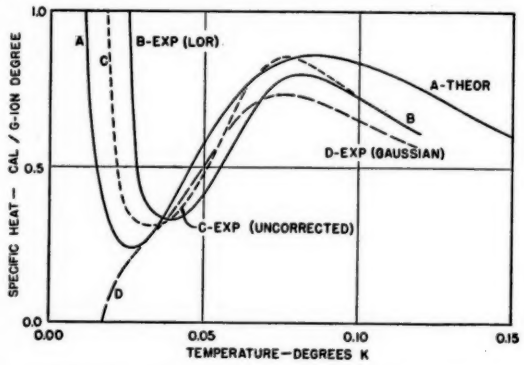


FIG. 6. Specific heat of potassium chromic alum for a splitting $\delta=0.20°=0.14$ cm^{-1}.

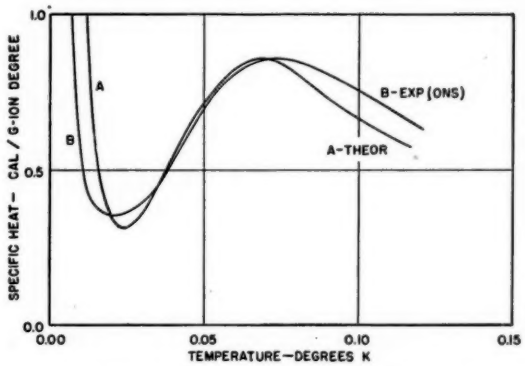


FIG. 7. Specific heat of potassium chromic alum for a splitting $\delta=0.17°=0.12$ cm^{-1}.

alum lie on a face-centered cubic lattice. Such a lattice may be regarded as four interlocking simple cubic lattices with the same lattice spacing as the original face centered lattice. With this picture, one finds that the trigonal axis is the same for all ions in a component simple cubic lattice but that a different body diagonal is preferred in each of the lattices.

We may thus assume that, in addition to the predominant cubic field, there is a small trigonal field along a body diagonal. There results a separation of states having components of moment $3/2$, $-3/2$ from those having components $1/2$, $-1/2$ along the trigonal axis. We find it necessary to suppose that the levels $\pm 3/2$ lie below $\pm 1/2$.

If we designate the splitting by δ as before, the partition function per ion in the crystalline field is

$$Z_c=2(1+e^{-\delta/kT}). \tag{24}$$

The characteristic temperature τ, found from (7) with $N=L/273, g=2, J=S=3/2$, is $\tau=0.0204$ deg. Then the specific heat is given by (22) with (24) and

$$\Omega=1.20\times 4Z_c^{-2}\left\{\left(\frac{3}{50}+\frac{223}{150}\frac{kT}{\delta}\right)+\left(\frac{88}{75}+\frac{8}{15}\frac{kT}{\delta}\right)e^{-\delta/kT}+\left(\frac{49}{150}-\frac{143}{150}\frac{kT}{\delta}\right)e^{-2\delta/kT}\right\}. \tag{25}$$

In Fig. 6, we show the calculated specific heat (curve A) for a splitting $\delta=0.20$ deg. $=0.14$ cm^{-1}. The uncorrected experimental curve is labeled C. The value of the splitting was chosen to give the best fit with the Lorentz corrected curve B obtained by using Eqs. (9), (12), (6) and

$$\gamma=(5Z_c/2)^{-1}\{(3+4kT/\delta)+(3-4kT/\delta)e^{-\delta/kT}\}. \tag{26}$$

Curve D, Fig. 6 represents the observed curve adjusted by means of the Gaussian susceptibility formula (15).

When the Onsager formula (10) is used to interpret the magnetic temperature, we find the best fit for a different splitting $\delta=0.17$ deg. $=0.12$ cm^{-1}. The calculated curve for this value of δ is shown by A, Fig. 7, along with the Onsager adjusted curve B.

It will be seen that, for the chromic alum, the fit between the calculated curve and the experimental curve corrected by the Onsager procedure is considerably closer than the fit with that corrected by the Lorentz method. The agreement between the theoretical and experimental specific heat adjusted with the Gaussian susceptibility formula is better than could be obtained with the ferric alum. There is definite disagreement, however, at the lowest temperatures.

CONCLUSION

The results which have been obtained in the preceding sections show that the method of crystalline potentials and the treatment of the magnetic dipole-dipole coupling provide a quantitative theory of the magnetic cooling method. The crystalline splitting found was of the ex-

pected order of magnitude.[8] There is, however, still some uncertainty as to the relative merits of the various susceptibility formulas. For this reason, it would be very desirable to have a precise and extensive investigation of the thermodynamic temperature scale below 1°K.[24] Then one could examine the temperature dependence of the entropy (or specific heat) and of the susceptibility, independently. Some preliminary work on the thermodynamic temperature scale has been reported by Giauque and MacDougall[26] and by Kürti and Simon.[4, 23] The former authors give the values of T for four values of T^* with $Gd(PMo_{12}O_{40})\cdot 30H_2O$ while the latter working with ferric alum show only two points. It must be emphasized that these experiments are exceedingly difficult as they combine the mechanical and calorimetric measurements discussed in the introduction. For this reason the present results are undoubtedly not final. We have been unable to reconcile their observations with the simple calculation of T^*/T as a series in $1/T$, as outlined in the introduction, for a reasonable choice of splitting. Giauque and MacDougall report that T^* is 22 percent *lower* than T at $T^*=0.15°$. If the splitting is not much smaller than that found for the previous hydrated gadolinium compounds, then we should expect T^* to be *greater* than T at this temperature. Part of the trouble may be due to their neglect of the Lorentz corrections in calculating the entropy from the initial field and temperature. Also part may be due to the difficulty, which they mention, of attaining thermal equilibrium between their induction heater and the salt. In this connection, Kürti and Simon's use of gamma-radiation[27] as the heat source seems to have an advantage.

For purposes of reference, we give in Table I, for various values of T, the percentage difference between T^* and T to be expected from our calculations.

The lowest temperature which has been so far reported is $T^*=0.0043°$ Curie, obtained by de Haas and Wiersma[3] with a mixture of potassium chromic alum and potassium aluminum alum. We find that this temperature is lowered to $T=0.0034°$K when corrected to the Kelvin scale. It makes no appreciable difference whether the Lorentz or Onsager treatment is used since the value $\tau=0.0013°$ for the diluted chromic alum is so much smaller than $T=0.0034°$. It is also immaterial whether the splitting is taken as $\delta=0.20°$ or $\delta=0.17°$.

We wish to thank Professor Van Vleck, who suggested this problem, for his very kind advice and aid.

[26] W. F. Giauque and D. P. MacDougall, Phys. Rev. **47**, 885(L) (1935).

[27] F. Simon, Nature 135, 763 (1935).

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The Free Energy of Diatomic Carbon Vapor

A. R. GORDON
Chemistry Department, University of Toronto, Toronto, Canada
(Received December 22, 1936)

An equation for the rotational state sum for a $^3\Pi$ molecule with intermediate a–b coupling is derived from Budó's expression for the rotational energy, and is used to compute the free energy of diatomic carbon vapor. Previous calculations of the equilibrium between C_2 and C in the vapor are discussed, and a revised equation for the equilibrium constant is obtained.

RECENTLY, a good deal of attention has been devoted in the literature to the interrelated problems of the heat of vaporization of carbon, the vapor pressure of carbon, and heat of dissociation of carbon monoxide.[1] Any interpretation of the vapor pressure data, however,

[1] See, for example, Herzberg, Nature **137**, 620 (1936); Goldfinger and Jeunehomme, Trans. Faraday Soc. **32**, 1591 (1936).

presupposes that the equilibrium between diatomic and monatomic carbon in the vapor is known, and since there has apparently been some uncertainty in the past as to this equilibrium, and since an exact calculation of the thermodynamic quantities for a $^3\Pi$ molecule such as C_2 has not been given, it appears desirable to deal with this latter problem specifically.

It is generally agreed[2] that the normal state of C_2 is an inverted $^3\Pi$ with intermediate coupling, for low values of the rotational energy case *a* being approached and for high values case *b*. The triplets are designated as $F_1(J)$, $F_2(J)$ and $F_3(J)$ where J (the total number of units of angular momentum) is equal to $K+1$, K, $K-1$ for F_1, F_2 and F_3, respectively, and $K(=1, 2, 3, \cdots)$ gives the number of units of angular momentum excluding electron spin. In a heteronuclear $^3\Pi$ molecule each of the states F_1, F_2, and F_3 would again be split into sublevels (Λ type doubling) but in a homonuclear molecule without nuclear spin (such as $C^{12}-C^{12}$), one of the two sub-levels of each doublet is missing. Budó[3] has obtained explicit expressions for the energy in the intermediate case, and has used these results to determine the spectroscopic constants[4] for C_2; he finds

$$F_1(J)=B[J^{*2}-(y_1+4J^{*2})^{\frac{1}{2}} -2(y_2-2J^{*2})/3(y_1+4J^{*2})] +D(J-\tfrac{1}{2})^4, \quad (1a)$$

$$F_2(J)=B[J^{*2}+4(y_2-2J^{*2})/3(y_1+4J^{*2})] +D(J+\tfrac{1}{2})^4, \quad (1b)$$

$$F_3(J)=B[J^{*2}+(y_1+4J^{*2})^{\frac{1}{2}} -2(y_2-2J^{*2})/3(y_1+4J^{*2})] +D(J+\tfrac{3}{2})^4, \quad (1c)$$

where $J^{*2}=J(J+1)$, $y_1=\Lambda^2Y(Y-4)+4/3$, $y_2=\Lambda^2Y(Y-1)-4/9$, $\Lambda=1$, $Y=A/B$, and A is the so-called magnetic coupling constant. Thus the contribution for any J to the state sum, if only the numerically most important terms are retained, is in general

$$(2J+1)\cdot e^{-J(J+1)/q}\cdot\{3+[y_1+4J(J+1)]/q^2 -3(Dhc/kT)(J+\tfrac{1}{2})^4\}, \quad (2)$$

where $q=kT/Bhc$.

An immediate summation of (2) over all values of J is subject to two restrictions: first, for $J=\Lambda-1=0$, the expression on the right of (1c) must be modified[5] as explained by Budó; second, the levels $F_1(0)$, $F_1(1)$ and $F_2(0)$ are missing since K must be equal to or greater than 1. It is easily verified that as far as the calculation of thermodynamic quantities for any temperature of experimental interest is concerned, the first restriction can be ignored, while the second can be taken into account by summing (2) over all values of J, i.e., $J=0, 1, 2, \cdots$, and then subtracting from the result the contribution of the three missing states. Proceeding then by conventional methods, the contribution of the normal electronic state is to a close enough approximation

$$3Q_V\cdot e^{F_1(2)hc/kT}\cdot(1+\beta_1\bar{v}+\beta_2\bar{v}^2) \times\{e^{1/4\,q_0}\cdot q_0[1+17/12q_0 +y_1/3q_0^2+\bar{d}+3(\bar{d})^2]-\Sigma'/3\} \quad (3)$$

where

$$Q_V=\Sigma\exp[-\epsilon_v hc/kT]=\Sigma\exp[-vw+(v^2+v)wx],$$
$$\bar{v}^n=(\Sigma v^n\cdot\exp[-\epsilon_v hc/kT])/Q_V, \quad w=hc\omega_e/kT,$$
$$q_0=kT/B_0hc, \quad B=B_0/(1+\beta_1 v+\beta_2 v^2),$$
$$\bar{d}=d_0(1+\delta\bar{v}), \quad d_0=(-2D_0/B_0)\cdot q_0,$$
$$\Sigma'=\exp[-F_1(0)hc/kT]+3\exp[-F_1(1)hc/kT] +\exp[-F_2(0)hc/kT].$$

The factor $\exp[F_1(2)hc/kT]$ serves to bring the zero of energy to that of the lowest observable rotational state, $J=2$ for F_1. The spectroscopic constants[2,4] for the normal state are: $\omega_e=1641.55$, $\omega_e x=11.67$, $B=1.6239-0.0171v$, $D=-6.4\times10^{-6}-0.2\times10^{-6}v$, $Y=-10.4$; thus $\beta_1=0.0105$, $\beta_2=1.1\times10^{-4}$, $\delta=0.053$. Numerical values of Q_V, $\bar{v}$ and $\bar{v}^2$ may be found at once from Gordon and Barnes' tables[6] for temperatures up to 3500°, or by means of their integral approximations for higher temperatures.

Of the lower lying excited electronic states for C_2, the position of only one relative to the ground state is known with certainty, *viz.* the $B^3\Pi$ state which constitutes the upper state of the Swan bands, 2.39 volts above the normal. Mulliken[7] predicts six additional electronic states less than 2.4 volts above the normal—$^3\Sigma$(0.55v), $^1\Delta$(1.35v),

[2] Weizel, *Bandenspektren* (1931) p. 333; Jevons, *Report on Band Spectra of Diatomic Molecules* (1932) p. 189.
[3] Budó, Zeits. f. Physik **96**, 219 (1935).
[4] Budó, Zeits. f. Physik **98**, 437 (1936).
[5] See p. 444 of reference 4.
[6] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).
[7] Mulliken, Rev. Mod. Phys. **3**, 1 (1932).

TABLE I.

$T°$ K	$-(F°-E_0°)/T$ for C_2	$-(F°-E_0°)/T$ for C	$\log (P_{C_2})/(P_C)^2$ $-\Delta E_0° = 125$ kcal.
2000	56.331	42.222	+7.52
3000	59.666	44.257	+2.80
4000	62.102	45.712	+0.42
5000	64.032	46.856	−1.02
6000	65.639	47.801	−2.00

$^1\Sigma(2.0v)$, $^1\Pi(2.1v)$, $^1\Sigma(2.15v)$ and $^3\Sigma(2.3v)$; of these, the 2.1 volt level is the lower state of the Deslandres-D'Azambuja bands, but the others have not been observed. Accordingly, in computing $(F°-E_0°)/T$ only the contributions of the normal $A^3\Pi$ state and the excited $B^3\Pi$ state were taken into account. An extended table of $(F°-E_0°)/T$ is hardly necessary, but values for a few temperatures are recorded in Table I. As verified by calculations for intermediate temperatures, the entries can be represented for the range 2000°–6000° within ±0.002 cal./deg. by the formula

$$-(F°-E_0°)/T=2.6757+3.5R\ln T - R\ln(1-\exp[-2318.0/T]) +1.978\times10^{-5}T+2.338\times10^{-9}T^2. \quad (4)$$

If Mulliken's estimates of the excitation energies of the other states is correct, the entries should be increased by 0.04 for 2000°, 0.21 for 4000° and 0.39 for 6000°.

Table I also gives the values of $(F°-E_0°)T$ for monatomic carbon vapor;[8] the resulting $\log K=\log (P_{C_2})/(P_C)^2$ can be represented for the temperatures of the table by the equation

$$\log K=-1.359-1.5\log T -\log(1-\exp[-2318/T])+2.73\times10^{-6}T -0.98\times10^{-9}T^2-\Delta E_0°/4.575T, \quad (5)$$

where $-\Delta E_0°$ is the energy of dissociation of the carbon molecule. Various estimates of this latter quantity have been made varying from 4 volts to 7 volts; Mulliken[7] gives 5.5 volts (~125 kcal.), which is the value assumed in computing the last column of the table.

[8] Bacher and Goudsmit, *Atomic Energy States* (1932), p. 101.

Vaughan and Kistiakowsky[9] in their calculation of this equilibrium used for the rotational state sum of C_2 $8\pi^2IkT/2h^2$ and then multiplied by an electronic multiplicity factor of 5, i.e., the rotational-electronic contribution of the normal state was taken to be 5/2 that of a heteronuclear $^1\Sigma$ molecule with the same moment of inertia. It is evident at once from inspection of (3) that to a fair approximation the contribution is 3 times that for the corresponding heteronuclear $^1\Sigma$ case. Marshall and Norton[10] give no details of the derivation of their equation (5), but their constant term, 1.462, corresponds roughly to Vaughan and Kistiakowsky's assumption. Kelley[11] quotes values of $-(F°-E_0°)/T$ from an unpublished thesis of Overstreet's; the entries are approximately 1.4 cal./deg. less than those in the second column of Table I, but no details are given which would serve to indicate the reason for the discrepancy. Goldfinger and Jeunehomme[1] take as the rotational contribution of C_2 $8\pi^2IkT/2h^2$, and then multiply by a multiplicity factor of 6—a justifiable approximation. Unfortunately, they used a moment of inertia 34.07×10^{-40}, twice that corresponding to $B=1.6239$; moreover, their equation for $R\ln K$ on p. 1595 is inconsistent[12] with their assumptions as to the quantum weight of C and the multiplicity of C_2, and is also in disagreement with the entries in their Table III.

In conclusion, it should perhaps be pointed out that before any interpretation of the extremely inconsistent vapor pressure data for carbon can be attempted, a trustworthy value for the heat of dissociation of C_2 is essential, and that until such a value is available, attempts to calculate the heat of vaporization of carbon from vapor pressure measurements can only lead to ambiguous results.

[9] Vaughan and Kistiakowsky, Phys. Rev. **40**, 457 (1932).
[10] Marshall and Norton, J. Am. Chem. Soc. **55**, 431 (1933).
[11] Kelley, U. S. Bureau of Mines Bulletin 383 (1935), p. 31.
[12] The term $R\ln 9$ in their equation should be $2R\ln 9 - R\ln 6$; the equation as printed with $I=34.07\times10^{-40}$ gives $\log K=7.97$ for 2000° and $\log K=-0.56$ for 5000° as compared with the entries +8.5 and +0.5 in their Table III.

Internal Volume and the Entropy of Vaporization of Liquids

O. K. RICE
University of North Carolina, Chapel Hill, North Carolina
(Received December 29, 1937)

An effective internal volume, V_e, of a liquid is defined by the equation $\Delta S = R \ln V_v/V_e$, where ΔS = entropy of vaporization, and V_v = molal volume of the vapor in equilibrium. A condition for equilibrium is found which gives ΔS in terms of V_e/V and dV_e/dV, where V is the actual molal volume of the liquid. The experimental data are considered in the light of this relationship, and the reason for the approximate validity of Trouton's or Hildebrand's rule is discussed. The nature of the relation between the internal and actual volume and its connection with the specific heat of the liquid is considered. Finally suggestions are made in way of explanation of the fact that entropies of vaporization of associated liquids are practically invariably high.

§1. INTRODUCTION

THE idea of the covolume of a liquid, that is, the portion of the volume in which the molecules are free to move, is one which was brought forward early in the development of the theory of liquids. It appears in, perhaps, its simplest form in van der Waals' equation, in which the molal volume, V, is corrected by subtraction of the "excluded volume," b. That this covolume, $V-b$, is closely related to the heat of vaporization has also long been realized. Thus it is shown in Nernst's *Theoretische Chemie* that, if one assumes van der Waals' equation to be correct, the heat of vaporization at equilibrium is given by the equation[1]

$$\Delta H = RT \ln [(V_v-b)/(V-b)], \qquad (1)$$

in which V_v is the molal volume of the vapor in equilibrium with the liquid, whose molal volume is V. The entropy of vaporization is accordingly

$$\Delta S = R \ln [(V_v-b)/(V-b)]. \qquad (2)$$

In view of the way the entropy of a gas depends upon its volume, it will be seen that the validity of Eq. (2) does not depend upon whether the vapor is in equilibrium with the liquid or not. The statement holds for all entropy equations of this general type, such as Eq. (3) below. However, unless otherwise specified, we shall write ΔS for the equilibrium entropy of vaporization.

The deduction of these equations in the form given depends upon the assumption that b is actually constant. Now b, the effective excluded volume, is equal to 4 times the volume of (one mole of) the gas molecules, and since the volume of a liquid can actually become less than this, b cannot be a true constant. Deviations begin to occur when V is around[2] $3b$, and they must be such that b appears to decrease.

Thus Eqs. (1) and (2) cannot be universally valid, but they suggest the definition of an effective volume, V_e, of the liquid by means of the equation[3]

$$\Delta S = R \ln (V_v/V_e). \qquad (3)$$

This quantity V_e will not be equal to $V-b$, even though b be considered to be a function of V, but in the region in which $[\partial(V-b)/\partial V]_T < 1$ it will also be true that

$$(\partial V_e/\partial V)_T < 1. \qquad (4)$$

It is interesting to note that, if we do assume that $(\partial V_e/\partial V)_T = 1$, the volume V_e and what Hildebrand calls the thermal pressure, P_t $(= P + (\partial E/\partial V)_T$, where P is applied pressure and E the energy of the system) have the same relation as the volume and pressure of a perfect gas. For we have the thermodynamic relationships

[1] English translation (Macmillan, 1923), p. 251. For more recent applications see Evans and Polanyi, Trans. Faraday Soc. **31**, 891 (1935); Horiuti, Zeits. f. Elektrochem. **39**, 22 (1933); Svenson, Ann. d. Physik, **87**, 424 (1928); also reference 3.

[2] Compare Loeb, *Kinetic Theory of Gases*, second edition (McGraw-Hill Book Co. 1934), p. 175.

[3] See Rice, J. Chem. Phys. **4**, 369–370 (1936). This equation assumes that V_v is large enough so that the vapor may be considered to be a perfect gas. The equation is essentially equivalent to Eq. (296) of Herzfeld, *Kinetische Theorie der Wärme* (Vieweg u. Sohn, Braunschweig, 1925).

$$P_t = P + (\partial E/\partial V)_T = T(\partial P/\partial T)_V = T(\partial S/\partial V)_T$$
$$= T(\partial S/\partial V_e)_T(\partial V_e/\partial V)_T$$
$$= (RT/V_e)(\partial V_e/\partial V)_T, \quad (5)$$

the last expression following from Eq. (3). Now if $(\partial V_e/\partial V)_T = 1$ it is seen that the required relationship holds. However, such a hypothetical "perfect" liquid does not exist.

§2. The Entropy of Vaporization of Normal Liquids

We shall now consider the factors which determine the entropy of vaporization of liquids in which the forces are of the van der Waals type, and in which the molecules are sufficiently symmetrical so that we are probably justified in supposing that they rotate freely in the liquid phase. If the external pressure, P, is of the order of a few atmospheres it is negligible, and we may write, from Eq. (5),

$$(\partial E/\partial V)_T = (RT/V_e)(\partial V_e/\partial V)_T, \quad (6)$$

and, in general, treat the liquid under its own vapor pressure as though it were at zero pressure.

On evaporation at equilibrium the change of entropy is related to the heat, ΔH, and the energy, ΔE, of vaporization by the equations

$$\Delta S = \Delta H/T = \Delta E/T + R. \quad (7)$$

If now we select the zero-point of energy so that the vapor has zero energy, we may set $\Delta E = -E$, and then eliminating T between (6) and (7) we obtain

$$\Delta S = -(ER/V_e)(\partial E/\partial V)_T^{-1}(\partial V_e/\partial V)_T + R. \quad (8)$$

In order to use this equation it is necessary to evaluate E as a function of V. Fortunately it seems to be possible to do this with some degree of approximation, for we may undoubtedly consider that the vaporization causes a change only in the *potential* energy of the system, and there are good experimental and theoretical reasons for believing that the change of E with V does not depend on whether the temperature changes or not, and is given over a certain range of values of V by an expression of the form[4]

$$dE/dV = a/V^2. \quad (9)$$

As (9) does not hold over the whole range of values of V from liquid to vapor, we cannot write $E = -a/V$, but instead set

$$E = -\gamma a/V, \quad (10)$$

where γ is a function of V, but never very different from 1. Eqs. (8), (9) and (10) give[5]

$$\Delta S = R \ln (V_v/V_e)$$
$$= R[\gamma(V/V_e)(\partial V_e/\partial V)_T + 1]. \quad (11)$$

By a few simple considerations we can see something about the form the function $\gamma(V/V_e) \times (\partial V_e/\partial V)_T$ must have in the case of molecules which are sufficiently near to being spherically symmetrical. It is reasonable to suppose that if the volume of the liquid is expressed in terms of the actual volume occupied by the molecules (measured by van der Waals' b) and V_e is expressed in the same terms, then all cases being reduced to geometrical similarity the effective volume should be the same function of the total volume for all cases. In other words

$$V_e/b = f(V/b) = f(v) \quad (12)$$

where $v = V/b$ and $f(v)$ is a universal function, from which it is clear that $(V/V_e)(\partial V_e/\partial V)_T$ should also be a universal function of v. Likewise γ should be such a function, so that we may write from (11)

$$\Delta S/R - 1 = \phi(v), \quad (13)$$

where ϕ is a universal function.

Table I.

Subs.	b.p. (°K)	V (cc) (at b.p.)	$\frac{\Delta S}{R} - 1$	V_e(cc)	V/V_e	V/V_e	$V_v/V \times 10^{-2}$
Ne	27.2	16.7	7.2	0.64	26	0.401	1.33
N_2	77.4	34.7	7.69	1.08	32	.385	1.83
CO	81.5	35.3	7.94	.90	39	.392	1.89
A	87.3	28.4	7.7	1.25	23	.379	2.52
O_2	90.1	28.1	8.10	.83	34	.377	2.63
CH_4	111.7	38.6	8.85	.49	79	.390	2.37
Kr	120.2	32	8.68	.63	51		3.1
Xe	166.0	42.5	8.92	.68	62	.378	3.21
HCl	188.1	30.5	9.32	.51	60	.35	5.05
HBr	206.1	37.4	9.28	.59	64		4.52
Rn	208	50	9.4	.52	98		3.4
HI	237.7	44.8	9.01	.87	51		4.34
Cl_2	238.5	45.5	8.3	1.86	24	.368	4.30
$SiCl_4$	330.7	121.3	9.95	.48	251		2.24
Br_2	331.9	53.5	10.02	.44	122	.394	5.08
CCl_4	349.9	104	9.48	.81	128	.377	2.76
$GeCl_4$	356.2	123	12.0	.066	1860		2.4
$SnCl_4$	387.2	132.9	9.4	.98	135		2.40

ΔS is calculated from ΔH values given in Bichowsky and Rossini's *Thermochemistry of Chemical Substances* (Reinhold Publishing Co. 1936). Other data from Landolt Börnstein, *Tabellen*, and *International Critical Tables*. All data are taken at, or corrected to, the boiling point.

[4] Hildebrand, *Solubility* (Reinhold Publishing Co. 1936), p. 98.

[5] It should be emphasized that Eq. (11) is a condition equation; namely, it is the condition that the external pressure be negligible.

It is generally assumed that the critical volume, V_c, is a measure of b. van der Waals' equation gives $V_c=3b$, but it is probably more nearly correct to set[6] $V_c=2b$. With the aid of this relation, Eq. (13) can be tested. Of course Eq. (13) can only be approximately correct, and that it is not exactly correct is readily seen from Table I, in which the various relevant quantities are given for a number of liquids at their boiling points, inasmuch as V/V_c appears to be approximately constant while $\Delta S/R-1$ is not. $\phi(v)$ may, however, be sensitive to small changes in v. This we can investigate by considering the temperature coefficient, provided we assume that the function ϕ is independent of temperature and that dV_e/dV does not depend upon whether there is a change in temperature or not.

We first note that

$$d\Delta S/dT=R[d\ln V_v/dT-d\ln V_e/dT]. \quad (14)$$

Now since we assume that the vapor is a perfect gas we have $d\ln V_v/dT=d\ln T/dT-d\ln P/dT$, where P is the vapor pressure. The last term can be evaluated sufficiently accurately by the Clapeyron equation, and we have $d\ln P/dT=\Delta S/RT$. And it is easy to see, from our assumption that dV_e/dV does not depend on whether T changes, and from Eq. (11), that $d\ln V_e/dT=(v/v_e)(dV_e/dV)\alpha=(\Delta S/R-1)\alpha/\gamma$, where $\alpha=V^{-1}dV/dT$ is the coefficient of expansion. Since, from the same assumption, $d/d\ln v=d/d\ln V=\alpha^{-1}d/dT$, we see, using these expressions and Eq. (13), and assuming γ is constant, that

$$d\ln\phi(v)/d\ln v=\alpha^{-1}d\ln(\Delta S-R)/dT=-(1/\alpha T+1/\gamma). \quad (15)$$

The right-hand side of (15) turns out to be around 3 for practically all substances. A range of v of about 10 percent would then account for the range of values of $\Delta S/R-1=\phi(v)$ observed in the liquids in Table I. In view of the difficulty in measuring the critical density there might be this much error in the observed values of v at the boiling point. However, if we make this assumption we run into a rather puzzling difficulty. It is seen that for the liquids listed V/V_e has approximately a tenfold range (if we neglect $GeCl_4$, which is probably in error). Now since $\gamma^{-1}\phi(v)=d\ln v_e/d\ln v$ (where $v_e=V_e/b$) we can calculate the range of v_e and hence the range of $v/v_e=V/V_e$ for a given range of v, and if v changes by 10 percent it is readily seen that with $\phi(v)$ in the neighborhood of 10 and γ always about 1, the ratio v/v_e should not vary more than two or threefold. This difficulty suggests that $\phi(v)$ differs slightly for various liquids. This, indeed, is also suggested by other facts, as we shall see immediately, but I have been unable to find any hypothesis regarding this variation of $\phi(v)$ which seems at all reasonable and at the same time is adequate to remove the difficulty just discussed.[7] If we ignore this difficulty, however, we are now in a position to consider the significance of such approximate empirical generalizations as Trouton's rule and its more accurate modification, Hildebrand's rule. Some such rule should follow from Eq. (11), which we now rewrite in the more convenient form

$$R\ln v_v/v_e=R[\phi(v)+1]. \quad (16)$$

Since v_e is a function of v this equation may be regarded as a condition equation on v, hence on v_e and V_e; thus the value of ΔS for any value of v_v or V_v is fixed by Eq. (16). If v_e (and hence $\phi(v)$) were the same function of v for all substances, then we should expect that all liquids would have the same value of the entropy of vaporization if it were measured at such a temperature that v_v were the same for all liquids. And we must remember that, at this temperature v and $v_v/v=V_v/V$, as well as ΔS would be fixed by Eq. (16) and have the same value for all liquids. Thus Trouton's rule would be expected to be obeyed if V_v/V were the same for all liquids at the boiling point, and Hildebrand's rule (which says that ΔS is the same for all liquids at such a temperature that the liquid is in equilibrium with vapor at some fixed value of V_v) is seen to require that V should be the same for all liquids at the Hildebrand temperature. Neglecting the small change in V on going from the Hildebrand temperature to the boiling point (or assuming, if V_v as chosen is far from the volume at the boiling point, that the change is about the same for all liquids) we see that

[6] Reference 2, p. 194.

[7] It is perhaps significant that the tetrahalides, which may not rotate freely in the liquid phase, are the liquids which are most out of line.

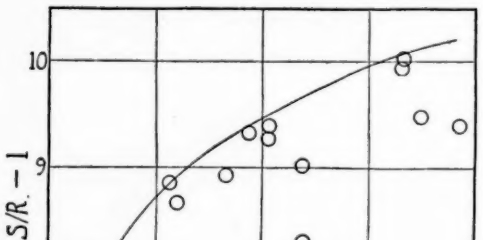

FIG. 1. $\Delta S/R-1$ as a function of T for the liquids of Table I, except $GeCl_4$. The curve is calculated from Table III, p. 103 of Hildebrand's *Solubility*, second edition, and gives the result to be expected from Hildebrand's rule, with benzene as the reference liquid. The use of benzene displaces the curve upward, but the shape should be approximately the same.

Hildebrand's rule demands that V should be practically the same for all liquids at the boiling point. Now, as may be seen from Table I, neither V_v/V nor V are the same for all liquids, so neither Trouton's rule nor Hildebrand's rule would hold if v_e were truly an absolutely definite universal function of v, but rather something in between. It is true that Hildebrand's rule is obeyed better than Trouton's rule, as will be clear from Fig. 1, but they do not after all differ very greatly from each other, and the approximate theoretical result may be considered to be in reasonably good agreement with the experimental facts.[8]

[8] Just as the present paper was being finished, I saw the preprint of the paper to be given at the Princeton symposium by Eyring and Hirschfelder, which parallels the development of §2 and §3 of this paper. However, the present paper takes up the questions involved from a somewhat different point of view, and discusses a different series of liquids, so it seems worthwhile to publish it in its entirety. If b of Eyring and Hirschfelder is considered to be the same for all liquids, then they may be said to have used a special form of $\phi(v)$, which has the advantage of giving approximately the correct magnitude for $\Delta S/R-1$, though all the difficulties as regards trends from liquid to liquid remain the same.

§3. The Quantity γ and the Heat Capacity

We can get at the evaluation of γ in another way, if we assume, as we have throughout, that the functional relationship between V_e and V is independent of the temperature,[9] and that the change of V_e with temperature is conditioned solely by the change of V. Suppose, now, we hold V_v constant and allow T to change. We may consider the change of entropy under these conditions in which equilibrium is not maintained, and write

$$(\partial\Delta S/\partial T)_{V_v}=-C/T \tag{17}$$

where C is equal to the specific heat per mole of the liquid at constant pressure minus the specific heat per mole of the vapor at constant volume. From (3), then (see statement directly following Eq. (2)), we see that

$$dR\ln V_e/dT=C/T. \tag{18}$$

Noting now that

$$d\ln V_e/dT=V_e^{-1}dV_e/dT=(V/V_e)(dV_e/dV)\alpha$$

we get from Eqs. (11) and (18)

$$C/\alpha RT=\gamma^{-1}(\Delta S/R-1), \tag{19}$$

where, in this equation, ΔS once more refers to

[9] In a paper which I saw in process of publication, Stearn and Eyring, J. Chem. Phys. **5**, 113 (1937), have treated the change of effective volume with temperature in a different way.

TABLE II.

Subs.	T(°K) (b.p.)	$\alpha\times10^3$	C_p (liq.) (calories per deg.)	C_v (gas)	C	$C/\alpha RT$	γ	$\gamma_{corr.}$	γ_H
N_2	77.4	5.88	13.64	4.97	8.67	9.6	0.80	1.19	
CO	81.5	5.2	14.43	4.97	9.46	11.2	0.71	1.01	
A	87.3	4.54	10.51	2.98	7.53	9.6	0.80	1.21	
O_2	90.1	4.14	12.99	4.98	8.01	10.8	0.75	1.16	
HBr	206.1	2.12	14.31	4.96	9.35	10.8	0.86	1.26	
Cl_2	238.5	1.61	16.25	5.82	10.43	13.7	0.60	0.85	
$SiCl_4$	330.7	1.83	35.2	20.25	15.0	12.5	0.80	1.00	0.98
Br_2	331.9	1.22	17.12	6.56	10.56	13.1	0.76	1.06	
CCl_4	349.9	1.36	32.43	19.11	13.32	14.1	0.67	0.87	0.93

Data from Landolt Börnstein, *Tabellen* and *International Critical Tables* (for α see especially density formulas in I.C.T.). On account of considerable discrepancies in the various values given, we note particularly that Pearson and Robinson's value of α was used for HBr and Latimer's value of C_p for $SiCl_4$.

the entropy of vaporization at equilibrium. Thus if γ is less than 1 we see that $C/\alpha RT$ should be greater than $\Delta S/R-1$, and a comparison of these quantities should enable us to evaluate γ. We have made this comparison in Table II for those substances in Table I for which data that seem reasonably reliable are at hand. It is seen that $C/\alpha RT$ is in general larger than $\Delta S/R-1$, but the relation between them is rather irregular, and if $(dV_e/dV)(V_e/V)^{-1}$ were calculated from $\Delta S/R-1$ by use of the values of γ obtained from Table II, the regularity in Fig. 1 would be lost. It seems likely that the irregularity is due to a large extent to experimental error in the determination of α.

We have the opportunity of comparing γ at the boiling point as obtained in the above manner with γ at 25°C (tabulated as γ_H) obtained by direct comparison of $(\partial E/\partial V)_T$ (as obtained by Hildebrand and his co-workers) with $\Delta E/V$ in the case of $SiCl_4$ and CCl_4. We have done this (reducing ΔH, from the tabulation of Bichowsky and Rossini, to 25°C and calculating ΔE) for these liquids and exhibited the results in Table II. It is seen that the agreement is only fair.

Note added, March, 1937: Doctors Eyring and Hirschfelder have called my attention to experimental data of Eucken and Hauck* which, as they remarked, shows that the assumption made at the beginning of §3 and the resulting equation

$$d \ln V_e/dT=(V/V_e)(dV_e/dV)\alpha \qquad (20)$$

cannot be exactly true. Eucken and Hauck have found that C_v for the liquid is greater than one would expect for the gas by about the amount that the specific heat of a three-dimensional oscillator differs from that of a monatomic gas. In other words, the liquid is more like a solid with respect to the translational motion of its molecules than it is like a gas. Now, we see from Eq. (3), holding V_v and V constant that

$$R(\partial \ln V_e/\partial T)_V=[C_v(\text{liq.})-C_v(\text{gas})]/T. \qquad (21)$$

Hence

$$d \ln V_e/dT=(\partial \ln V_e/\partial T)_V+(\partial \ln V_e/\partial V)_T(dV/dT)$$
$$=C_v(\text{liq.})/RT-C_V(\text{gas})/RT+(V/V_e)(\partial V_e/\partial V)_T\alpha, \qquad (22)$$

it being understood that $V^{-1}(dV/dT)=\alpha$ refers to the expansion of the liquid at zero pressure, or, what amounts to the same thing, under its vapor pressure. Combining (22) with (18) and (11) we get in place of (19)

$$C'/\alpha RT=\gamma_{\text{corr.}}^{-1}(\Delta S/R-1), \qquad (23)$$

where $C'=C_p(\text{liq.})-C_v(\text{liq.})$ and $\gamma_{\text{corr.}}$ is the true value of γ, as contrasted to the value γ tabulated in Table II.

* Zeits. f. physik. Chemie **134,** 161 (1928).

We have added a column of $\gamma_{\text{corr.}}$ obtained (except in the case of argon, where C_v(liq.) was taken directly from Eucken and Hauck's data, and the cases of O_2, N_2 and CO, where Eucken and Hauck's value for air was used) by assuming that $C_v(\text{liq.})-C_v(\text{gas})=3R/2=2.98$ calories per mole. It is to be noted that there is now reasonably good agreement between $\gamma_{\text{corr.}}$ and γ_H for $SiCl_4$ and CCl_4.

Since the assumption of Eq. (20) was used in Eq. (15), we must, in order to be consistent, use the uncorrected value of γ when applying Eq. (15). If this is done the assumption embodied in Eq. (20) cancels out. The assumption remains that $d\phi(v)/dv$ is independent of temperature changes. If we can assume that γ is approximately independent of temperature (and since it does not vary greatly at all, this seems reasonable) this will be true if $d \ln v_e/d \ln v = V(\partial S/\partial V)_T R^{-1}$ is independent of temperature. Now $(\partial S/\partial V)_T$ is independent of temperature if $C_v(\text{liq.})-C_v(\text{gas})$ is independent of volume. The measurements of Eucken and Hauck, while not extensive enough to prove this definitely, indicate that probably $C_v(\text{liq.})-C_v(\text{gas})$ is constant for simple liquids at the volumes which prevail at and below the boiling point. Therefore, we believe that we can conclude that Eq. (15) is valid if the uncorrected value of γ is used.

§4. Associated Liquids

There are a number of substances which have abnormally high entropies of vaporization, and it has long been customary to assume that that is due to molecular association. A similar effect might be expected if the molecules were prevented from rotating by mere mechanical interference. Such phenomena undoubtedly result in a decrease of the entropy of a liquid, and it is assumed that the substance must acquire the extra entropy in evaporating. This would be undoubtedly true if the substance boiled at the same temperature as if it were not associated or its rotation unimpeded, but as a matter of fact the boiling point is higher, being determined ultimately by Eq. (8), and there is no reason why the entropy of association might not be balanced or overcome by changes in other types of entropy at the point of equilibrium.

In the case of an associated liquid the situation is complicated by the fact that we cannot use Eq. (11) for Eq. (9) will not be followed when the energy of association is included, and γ is thus unknown. However, we can gain some understanding of the fact that the ΔS of vaporization is higher than normal at the boiling point, or at least see the conditions which must hold for this to be true. Let us suppose that we

wish to know the entropy of vaporization at a temperature, T, such that the liquid is in equilibrium with vapor at a definite pressure, say, 1 atmosphere. If the liquid were *not* associated, this equilibrium would take place at a temperature T_0 and the effective volume of the liquid would be V_e'. The entropy of vaporization would be, say, $\Delta S'=\Delta E'/T_0+R$; in the actual liquid, however, there is an extra entropy of vaporization due to the necessity of first dissociating the molecules. Call it $\Delta S''$ and the corresponding extra energy of vaporization $\Delta E''$. The total entropies and energies of vaporization are thus given by $\Delta S=\Delta S'+\Delta S''$ and $\Delta E=\Delta E'+\Delta E''$. We must, at any temperature, have $\Delta E''/T>\Delta S''$, else the liquid would not be associated. Hence, we see that, at T_0 we have for the free energy of vaporization at atmosphere (what is, in itself, obvious)

$$\Delta F=\Delta E+RT-T\Delta S>0. \tag{24}$$

As the liquid warms up the free energy decreases. We have the general thermodynamic equation

$$d\Delta F/dT=-\Delta S. \tag{25}$$

So equilibrium will occur at a higher temperature. At the same time ΔS will change. We have

$$d\Delta S/dT=\Delta C_p/T. \tag{26}$$

Since C_p for the vapor is less than that for the liquid, ΔS also decreases with the temperature. The question we now have to answer is: Will ΔF reach zero before ΔS reaches the value which $\Delta S'$ had at T_0 (which is, of course, the normal entropy of vaporization of an unassociated liquid)? This will generally be the case if, at $T=T_0$,

$$\frac{-d\Delta F/dT}{\Delta F}>\frac{-d\Delta S/dT}{\Delta S-\Delta S'}, \tag{27}$$

or

$$\frac{\Delta S}{\Delta F}>\frac{-\Delta C_p}{T(\Delta S-\Delta S')}. \tag{28}$$

Putting in the values of these quantities at $T=T_0$, we can write, specifically,

$$\frac{\Delta S}{\Delta E''-T_0\Delta S''}>\frac{-\Delta C_p}{T_0\Delta S''} \tag{29}$$

or we must have

$$-\frac{\Delta S}{\Delta C_p}>\frac{\Delta E''-T_0\Delta S''}{T_0\Delta S''}. \tag{30}$$

Now ΔS will always be considerably greater than $-\Delta C_p$, for in case of any appreciable tendency toward association ΔS will be considerably greater than 20, while, with water, methyl and ethyl alcohols, typical associated liquids, $-\Delta C_p$ is not over 10 or 11 calories per degree per mole.[10] The observed energy of vaporization at the boiling point will, therefore, be greater than normal unless $\Delta E''$ is three or four times as great as $T_0\Delta S''$. If this were the case, and $\Delta S''$ were at all large, we should expect appreciable association in the gas phase. For example, if $\Delta S''=10$ and $T_0=300$ and $\Delta E''=3T_0\Delta S''$, we have $\Delta E''=9000$, which would correspond to an energy of dissociation of the double molecules of about 18,000. This is greater than the energy of dissociation of N_2O_4.

I wish to thank Professor J. H. Hildebrand for helpful discussions during the early stages of the preparation of this paper.

[10] Landolt-Börnstein, *Tabellen*. The specific heat values for the vapors of methyl and ethyl alcohols obtained from the data of Fiock, Ginnings, and Holton, Nat. Bur. Stand. J. Research **6**, 886 (1931) are very low. This is probably because they measured the heat content of the saturated vapor, and the number of associated molecules, while small, is not entirely negligible and increases as the temperature and pressure go up. In our argument we neglect the presence of associated molecules in the vapor, which in these liquids is the correct procedure for our purposes.

The Entropies of *n*-Butane and Isobutane, with Some Heat Capacity Data for Isobutane

GEORGE S. PARKS, C. HOWARD SHOMATE, W. D. KENNEDY AND BRYCE L. CRAWFORD, JR.
Department of Chemistry, Stanford University, California

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The entropies of *n*-butane ($S_{298}°=75.8$ e.u.) and isobutane ($S_{298}°=70.0$ e.u.) have been calculated from thermal data by the third law of thermodynamics. In this connection, heat capacity data for isobutane over the temperature range 79°–261°K have been obtained by the Nernst method and also, as a partial basis for these calculations, the mode of extrapolating entropies below liquid air temperatures has been critically examined. The discrepancies between these new results and the corresponding entropies obtained by statistical methods appear too large to be accounted for by errors in the thermal data or extrapolations involved. The thermodynamics of the isomerization reaction is briefly considered.

THE entropies of *n*-butane and isobutane, as well as of a number of other hydrocarbons, have recently been calculated by Kassel[1] by statistical methods. Omitting the contribution due to nuclear spin, he obtained 78.16 e.u. for *n*-butane and 74.04 e.u. for the *iso* compound at 298.1°K. Huffman, Parks, and Barmore[2] had previously measured the heat capacities of *n*-butane from 67° up to the boiling point and had calculated by the third law of thermodynamics an entropy value of 74.5 e.u. (erroneously reported as 74.4 e.u.). This discrepancy of nearly 3.7 e.u. between his value and the third law result Kassel then attributed to either an error in the extrapolation from 90°K to 0° by Parks, Huffman and Barmore or to "a zero-point entropy of the crystals caused by lack of equilibrium at the lower temperatures."

In this investigation we have critically reexamined the entropy calculations of Huffman, Parks and Barmore for *n*-butane and have thereby obtained $S_{298}°=75.8$ e.u. as a more probable third law result. At the same time we have measured the heat capacities of isobutane from 79°K up to its boiling point and have likewise employed these data in calculating a value of $S_{298}°=70.0$ e.u. Thus the discrepancies between the third law entropies and the results of Kassel's statistical calculations continue to be pronounced.

[1] L. S. Kassel, J. Chem. Phys. **4**, 276 (1936).
[2] H. M. Huffman, G. S. Parks, and Mark Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).

THE HEAT CAPACITY DATA FOR ISOBUTANE

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the heat of fusion of isobutane. The apparatus and details of experimental procedure have been fully described in other places.[3] In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is probably less than 0.7 percent; the fortuitous errors were usually under 0.25 percent. The results have been expressed in terms of the *defined* calorie (=4.185 absolute joules) per gram molecule, with all weights reduced to a vacuum basis.

The isobutane sample was specially prepared for us in the laboratory of the Shell Development Company by hydrogenation of very pure isobutane and by a subsequent series of careful fractional distillations of the resulting paraffin. From the change in melting point during the fusion determinations we estimated its purity to be about 99.7 mole percent. Incidentally, the melting point of pure isobutane was found to be 113.2°K, or almost 15° below the figure given in the *International Critical Tables*.[4]

Our various specific heat values (C_p) for the crystalline and liquid isobutane are given in Table I and are also represented graphically in Fig. 1. In addition, two independent determina-

[3] G. S. Parks, J. Am. Chem. Soc. **47**, 338 (1925); also G. S. Parks and K. K. Kelley, J. Phys. Chem. **30**, 47 (1926).
[4] *International Critical Tables* (1926), Vol. I, p. 188.

tions of the heat of fusion were made and these are given in Table II.

Calculation of the Entropies

As the specific heat determinations on *n*-butane by Huffman, Parks and Barmore did not go below 67°K and those on isobutane in the present study extended to only 79°K, a fairly reliable method of extrapolating the entropies to the absolute zero is essential. In the present case we have employed the method of Kelley, Parks and Huffman.[5]

The extrapolation method

Kelley, Parks and Huffman in 1929 made a comparative study of the heat capacity curves for twelve organic compounds for which experimental data were available between 15° and 120°K. Seven of these compounds were aliphatic; incidentally these all contained oxygen and were more or less polar in character. The remaining five compounds possessed carbocyclic molecules and were either nonpolar or only moderately polar. While all twelve substances exhibited essentially similar heat capacity-temperature curves, those for the seven aliphatic compounds tended to fall off somewhat more rapidly with decreasing temperatures than those for the cyclic compounds. Subsequently these two groups were designated as "class I" and "class II," respectively. It was then an easy matter to develop an ideal or "standard" curve for each class, such that at any temperature T the actual heat capacity (C_p) of a compound was reasonably well represented by the equation

$$C_p=(A+BT)C_p^\circ, \tag{1}$$

where A and B were empirical constants characteristic of the particular compound and C_p° was the heat capacity on the standard curve at the temperature in question. Accordingly the entropy of the compound at this particular temperature becomes simply

$$S_T=AS_T^\circ+B\int_0^T C_p^\circ dT, \tag{2}$$

where S_T° is the entropy increment corresponding to the standard curve from 0°K to T and $\int_0^T C_p^\circ dT$ is the increase in the standard heat content. To evaluate properly the empirical constants, A and B, it is simply necessary to substitute in Eq. (1) two reliable experimental values for C_p at different temperatures, such as 80° and 110°K.

Since 1929 this method has been extensively utilized in third law calculations for estimating

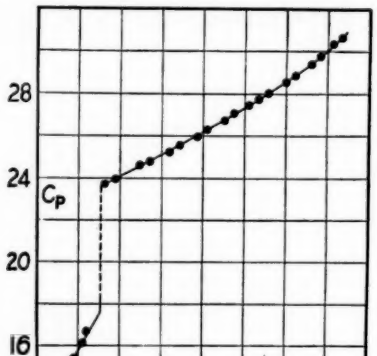

Fig. 1. The molal heat capacity of isobutane plotted against the absolute temperature.

Table I. *Specific heats of isobutane in cal. per degree. (Molecular weight, 58.077.)*

T, °K	C_p per gram	C_p per mole	T, °K	C_p per gram	C_p per mole
Crystals			*Liquid*		
81.3	0.2267	13.17	171.5	0.4471	25.97
86.0	.2379	13.82	177.3	.4528	26.30
91.2	.2506	14.55	187.8	.4602	26.73
97.3	.2649	15.38	193.5	.4664	27.09
102.5	.2776	16.12	202.7	.4733	27.49
104.8	.2872	16.68	208.5	.4779	27.75
Liquid			214.3	.4824	28.02
115.4	0.4085	23.72	225.0	.4917	28.56
122.1	.4122	23.94	230.6	.4973	28.88
136.5	.4239	24.62	240.2	.5065	29.42
142.8	.4270	24.80	245.4	.5127	29.78
154.6	.4345	25.23	253.0	.5231	30.38
160.8	.4402	25.57	258.3	.5283	30.68

Table II. *Fusion data for isobutane at 113.2°K.*

	Heat of Fusion cal./gram	cal./mole
First determination	18.50	1074.5
Second determination	18.53	1075.9
Mean	18.51	1075.2

[5] K. K. Kelley, G. S. Parks and H. M. Huffman, J. Phys. Chem. **33**, 1802 (1929).

the entropy increments of organic compounds in going from 0° to 80° or 90°K. However, only recently have experimental heat capacity data become available for further testing its applicability. The specific heat measurements of Giauque and Egan[6] on carbon dioxide, of Bekkedahl and Mathęson[7] on "crystalline rubber hydrocarbon" (i.e., polymerized C_5H_8), of Aston and Messerly[8] on tetramethylmethane, of Ahlberg, Blanchard and Lundberg[9] on benzene, and of Southard and Brickwedde[10] on naphthalene have now enabled us to make the comparisons given in Table III.

TABLE III. *New tests of the extrapolation method for entropies. (Expressed in cal./degree per formula weight.)*

Substance	Experimental Value of S_{90}	Calculated			
		Class I		Class II	
		S_{90}	Error	S_{90}	Error
CO_2 crystals	8.12	8.24	+0.12	9.33	+1.21
C_5H_8 unit	8.37	7.47	−0.90	8.32	−0.05
C_5H_{12}*	12.02	9.50	−2.52	11.05	−0.97
C_6H_6	10.89	9.97	−0.92	11.35	+0.46
$C_{10}H_8$	13.52	11.27	−2.25	13.69	+0.17

* The data in this line apply at 70°K.

The "experimental S_{90}" values tabulated here were all obtained from the measured specific heats by graphical integration and the corresponding "calculated" values, except in the case of tetramethylmethane, were derived by Eq. (2) with the aid of the experimental heat capacities at 90° and 120°K. Tetramethylmethane, a rather unique organic compound, exhibits a transition of some sort in the neighborhood of 140°K and its measured specific heats appear to be more or less affected by this transition down even to about 75°. As a consequence its heat capacity curve for the crystals is far from standard and we have here estimated its entropy at 70° (instead of 90°) by employing its C_p value at 70° and assuming that in this case the value for B in Eq. (2) is zero.

From these comparisons of experimental and calculated entropies it is evident that the class II constants hold well for benzene and naphthalene and the class I constants for carbon dioxide. Such findings, of course, might have been anticipated from the earlier study of Kelley, Parks and Huffman. However, the class II curve also fits the data for the aliphatic isoprene unit very well and comes closer than the class I curve in giving an approximate result for tetramethylmethane. It thus appears probable that in entropy extrapolations the class II constants should be applied to all hydrocarbons,* whether aliphatic or cyclic, in preference to the class I constants, which probably apply solely to highly oxygenated or polar molecules.[11]

This view is also supported by the fact that the experimental heat capacities for crystalline *n*-butane between 67° and 100°K fit the standard class II curve very closely, with values for $A=0.973$ and $B=0.00071$. The corresponding entropy extrapolation below 67°K yields 9.88 e.u. per mole, a result which would be good to ±0.86 e.u. even if the extrapolation method should be in error here by as large a percentage as in the case of the highly anomalous tetramethylmethane.

By a similar extrapolation with the class II constants we have found 10.52 e.u. per mole for the increment in entropy of crystalline isobutane between 0° and 79°K. Here again our experimental heat capacities conform to Eq. (2) with remarkable fidelity. In spite of this fact, however, we feel that isobutane, closely related structurally to tetramethylmethane, may show at temperatures below 79°K a somewhat similar

[6] W. F. Giauque and C. J. Egan, J. Chem. Phys. **5**, 45 (1937).

[7] N. Bekkedahl and H. Matheson, Nat. Bur. Stand. J. Research **15**, 503 (1935).

[8] J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).

[9] Ahlberg, Blanchard and Lundberg, J. Chem. Phys. (to be published); also referred to by Lord and Andrews, J. Phys. Chem. **41**, 156 (1937).

[10] J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc. **55**, 4378 (1933).

* *Note added to the proof.*—Since the preparation of this manuscript R. K. Witt and J. D. Kemp [J. Am. Chem. Soc. **59**, 273 (1937)] have published heat capacity values for crystalline ethane between 15° and the melting point, 89.87°K. Their data fit the class II curve quite well from 80° to 40° and yield, with the class II constants, a "calculated" entropy of 11.14 e.u. at 89.87°K. The corresponding experimental result is 10.74 e. u., a difference of 0.40 e. u.

[11] It should be noted here that the class I constants have been previously employed in this laboratory in all entropy extrapolations for aliphatic hydrocarbons. Accordingly, such entropies are not strictly comparable with those which are to be presented now for the two butanes; and for proper comparison these earlier extrapolations below 80° or 90°K will have to be revised upwards (by an average of perhaps 10 percent) with the aid of the class II constants.

TABLE IV. *The entropy of n-butane from calorimetric data (in calories per degree per mole).*

0°–67°K, Extrapolation (method of K. P. and H.)	9.88±0.7	
67°–134.1°K, Crystals (graphical)	16.23	±0.2
Fusion 1044.3/134.1	7.79	
134.1°–272.5°K, Liquid (graphical)	20.25	
Vaporization 5324/272.5	19.54±0.2	
272.5°–298.1°K, Gas (average $C_p=21.6$)	1.95	±0.1
Correction for gas imperfection	0.14	
Entropy of ideal gas at 1 atmos. and 298.1°K	75.8±0.8	

TABLE V. *The entropy of isobutane from calorimetric data (in calories per degree per mole).*

0°–79°K, Extrapolation (method of K. P. and H.)	10.52±1.0	
79°–113.2°K, Crystals (graphical)	5.43	±0.2
Fusion 1075.2/113.2	9.50	
113.2°–260.9°K. Liquid (graphical)	22.05	
Vaporization 5095/260.9	19.53±0.2	
260.9°–298.1°K, Gas (average $C_p=21.3$)	2.84	±0.2
Correction for gas imperfection	0.12	
Entropy of ideal gas at 1 atmos. and 298.1°K	70.0±1.1	

positive deviation from our extrapolation formulas. In such an event this estimate of $S_{79}=10.52$ e.u. may possibly be about one entropy unit too small.

The entropy of *n*-butane

With the aid of the extrapolation result given in the preceding section we have now recalculated the molal entropy of *n*-butane as an ideal gas at 298.1°K and 1 atmos. fugacity. The essential data are given in Table IV.

The entropy increments between 67° and 272.5°K have been obtained directly from the heat capacity data of Huffman, Parks and Barmore[2] for the crystalline and liquid states. These data have been carefully rechecked and the specific heat values above 220° slightly altered, since we have recently found that this laboratory's earlier specific heat determinations on hydrocarbons between 220° and 300°K were over-corrected (by a fraction of 1 percent) for certain radiation losses.

The entropy of vaporization (20.44 e.u.) adopted previously by Huffman, Parks and Barmore was undoubtedly too large. It was obtained by use of Burrell and Robertson's[12] approximate value for the heat of vaporization, which had been calculated from vapor pressure data by assuming perfect gas behavior of *n*-butane vapor and neglecting the volume of the liquid in the Clausius equation. By taking into account gas imperfection and the liquid volume, we now estimate $\Delta S=19.60$ (±0.3) e.u. from Burrell and Robertson's data. However, the direct calorimetric determination of Dana, Jenkins, Burdick and Timm[13] for the heat of vaporization of this substance is much more reliable. Adoption of their value for this heat effect and for the boiling point gives us the tabulated entropy of vaporization. It is undoubtedly very near the truth, since Aston and Messerly[8] have recently found 19.24 e.u. for the vaporization entropy of tetramethylmethane and the data of Sage, Lacey and Schaafsma[14] yield 19.61 e.u. for *n*-pentane.

The small entropy correction for gas imperfection has been made with Berthelot's equation according to the method of Giauque and Wiebe.[15] The tabulated increment for gaseous butane between 272.5° and 298.1°K has been calculated on the assumption of a constant C_p of 21.6 cal. per mole, this being the value indicated for the mean temperature (285.3°K) in Fig. 36 of Sage and Lacey's recent paper.[16]

Considering the various sources of error in this third law calculation, we believe that our final value of $S_{298}°=75.8\pm0.8$ e.u. probably errs on the side of being a trifle high.

The entropy of isobutane

The essential contributions in the calculation of the entropy of isobutane by the third law are summarized in Table V. The increment for the crystals between 79° and 113.2°, the entropy of fusion and the increment for the liquid up to 260.9°K have been derived directly from the heat capacity data presented in the present paper. The entropy of vaporization has been obtained by use of the boiling point and corresponding heat of vaporization of isobutane reported by Dana, Jenkins, Burdick and Timm.[13]

[12] G. A. Burrell and I. W. Robertson, J. Am. Chem. Soc. **37**, 2188 (1915).

[13] L. I. Dana, A. C. Jenkins, J. N. Burdick and R. C. Timm, Refrigerating Eng. **12**, 387 (1926).

[14] B. H. Sage, W. N. Lacey and J. G. Schaafsma, Ind. Eng. Chem. **27**, 48 (1935).

[15] W. F. Giauque and R. Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).

[16] B. H. Sage and W. N. Lacey, Ind. Eng. Chem. **27**, 1484 (1935).

The correction for gas imperfection has been calculated by the method of Giauque and Wiebe.[15] The increment for the gas between 260.9° and 298.1° has been calculated by the assumption of a constant C_p of 21.3 cal. per mole for isobutane, an estimate which we derived from a consideration of Sage and Lacey's[16] specific heat curve for gaseous *n*-butane. The final value $S_{298}°=70.0$ e.u. is possibly a little too low.

Conclusion

On the assumption of the third law of thermodynamics we have now calculated $S_{298}°=75.8\pm0.8$ e.u. for *n*-butane and $S_{298}°=70.0\pm1.1$ e.u. for isobutane. These values are lower than the corresponding ones calculated by Kassel[1] by 2.36 e.u. and 4.04 e.u., respectively; and the differences appear to be too great to be accounted for on the basis of errors in the thermal data or in the extrapolations from liquid-air temperatures down to the absolute zero.

A similar entropy discrepancy has been described by Kemp and Pitzer[17] in the case of ethane and by Aston and Messerly[8] in the case of tetramethylmethane. The situation, therefore, is apparently a general one and indicates that there is some fundamental error in either the third law or the statistical entropies. The difficulty may lie in an incorrect assumption of free rotation about the C−C bond in the statistical method, as already suggested by Kemp and Pitzer, or it may arise from the presence of a finite entropy at the absolute zero in all these crystalline hydrocarbons, as suggested by Kassel.

[17] J. D. Kemp and K. S. Pitzer, J. Chem. Phys. **4**, 749 (1936).

The Isomerization of *n*-Butane

We are now in a position to consider the thermodynamics of the isomerization reaction

$$n\text{-}C_4H_{10}\rightarrow iso\text{-}C_4H_{10}.$$

Rossini[18] from his extremely accurate combustion data has calculated $\Delta H_{298}°=-1630$ (±150) cal. for this reaction and our present entropy values yield $\Delta S_{298}°=-5.8$ (±1.2) e.u. Hence, $\Delta F_{298}°=-1630+(298.1)(5.8)=100$ (±400) cal. Thus at room temperature the *n*-butane is, perhaps, very slightly more stable than the *iso* compound.

At elevated temperatures, however, the comparative stability of the normal compound is probably much more pronounced. As Beeck[19] has recently indicated the heat capacities of these two hydrocarbons in the gaseous state must be almost identical. Hence, the general free energy equation for this isomerization reaction becomes

$$\Delta F°=-1630+5.8T. \qquad (3)$$

Thus at 800°K (i.e., 527°C) $\Delta F°=3010$ cal. and an equilibrium mixture of the two butanes should contain 87 percent of the normal and 13 percent of the *iso* compound.

Acknowledgment

Before concluding, we wish to take this opportunity to thank the Shell Development Company and the Standard Oil Company of California for financial assistance in this investigation.

[18] F. D. Rossini, J. Chem. Phys. **3**, 438 (1935).
[19] O. Beeck, J. Chem. Phys. **4**, 680 (1936).

Studies on Glass

XV. The Viscosity and Rigidity of Glucose Glass

GEORGE S. PARKS AND JOHN D. REAGH
Department of Chemistry, Stanford University, California

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By an electromagnetic torsion method, in which glucose glass threads were substituted for the phosphor-bronze suspension in a d'Arsonval galvanometer, the rigidity and viscosity of glucose glass have been measured between 12° and 37.5°C. The rigidity values were fairly constant around 2.5 (10^{10}) dynes per cm² between 12° and 30° but decreased rapidly above the latter temperature. The viscosity values ranged between 10^{15} and 10^{10} poises. These values decreased rapidly with rising temperatures but also depended greatly on the previous history of the glass threads, i.e., the extent to which the threads had been annealed and the amount of previous working to which they had been subjected. This finding suggests the existence of a series of glassy states for a substance such as amorphous glucose.

IF a cylindrical body is subjected at one end to a torsional couple while the other end is held stationary, there may result within the body (a) an elastic displacement or (b) viscous flow or (c) a combination of these two phenomena. For the elastic displacement we have the relation

$$R=2Cl/\pi r^4\theta, \qquad (1)$$

where R is the modulus of rigidity of the material of which the cylindrical body is composed, l and r are, respectively, the length and radius of the cylinder, θ is the angular displacement of the movable end, and C is the torsional couple. Correspondingly for viscous flow, the coefficient of viscosity is given by the equation

$$\eta=2Cl/\pi r^4\omega, \qquad (2)$$

where ω is the angular velocity of flow with the couple C. With some materials, under suitable conditions, both elastic displacement and viscous flow take place to a very appreciable extent. We have found that such is the case with glucose glass within the temperature range 12°–35°C.

PREPARATION OF THE GLASS SAMPLES

In the present study the glucose glass was used in the form of cylindrical threads, 10 to 14 cm long and 0.05 to 0.12 cm in diameter. Liquid glucose was first prepared by melting crystals of either Pfanstiehl C. P. α glucose or a special National Bureau of Standards material ("Sample 41") in accordance with the procedure of Parks, Huffman and Cattoir.[1] Then by dipping a small glass rod into a sample of this liquid, undercooled to about 100°, and withdrawing it slowly, threads of glassy glucose, 20 to 40 cm long, could be readily obtained. Perhaps a quarter of these were almost perfectly cylindrical with a cross section uniform to ±4 percent, a fact which was fairly clear from a careful inspection and which always was subsequently verified by weighing small sections taken from different portions of the thread.

The radius of these glass threads was readily calculated from the mass of a given length and the density value of 1.523 g per cc at 20°, given by Parks, Huffman and Cattoir. Before use the threads were kept in a vacuum desiccator over phosphorous pentoxide. The glass products of the two different samples of glucose crystals were apparently the same and the values of their properties depended only on the extent of their annealing and on their previous mechanical treatment.

THE TORSION APPARATUS

In the measurements these glucose threads were subjected to an electromagnetic torsional couple by substituting them for the phosphor-bronze suspension in a Leeds-Northrup type P d'Arsonval galvanometer of 116 ohms internal resistance. To complete the electric circuit

[1] G. S. Parks, H. M. Huffman and F. R. Cattoir, J. Phys. Chem. **32**, 1366 (1928).

through the movable galvanometer coil, a short spiral of very fine phosphor-bronze wire was then connected to the coil from below to function in place of the usual metallic suspension. The galvanometer was next connected in series with a two-volt battery, an adjustable resistance box and a milliammeter. The deflections of the galvanometer were read with a telescope and curved millimeter scale, placed at a distance of 49 cm from the movable coil.

The torsional couples corresponding to the use of various current strengths were readily evaluated, by Eq. (1), in a calibration of the galvanometer in which suspensions of B. and S. No. 28 copper wire and No. 30 Chromel wire were employed and the current and corresponding deflections were measured. For this purpose the moduli of rigidity of these copper and Chromel wires were previously determined by measurement of the periods of angular oscillation when a brass rod of known moment of inertia was suspended from definite lengths of the wires in question.[2]

In the actual experiments with glucose thread suspensions the scale deflections of the galvanometer were read with the telescope to 0.5 mm at intervals over a period of twenty to forty minutes while the electric current was on; then the current was cut off and the elastic return of the galvanometer was noted, sometimes over a period of several hours. The character of the deflections in a typical case (a determination at 19.6°C) is shown in Fig. 1, where the scale deflection in cm has been plotted against the time in minutes. With the imposition of the electromagnetic couple there was an immediate elastic deflection θ_1, which was usually measured within an interval of 15 to 20 seconds. This was followed by a flow which was partly simple viscous and partly elastico-viscous in character and which is represented by the deflection θ_2. At the end of 31 minutes in this case the current was cut off and there followed an immediate elastic return and an elastico-viscous return in the course of 80 minutes, which together were equal to the quantity $\theta_1+\theta_2-\theta_3$. The permanent viscous flow due to the imposition of the electromagnetic couple for 31 minutes was represented by θ_3.

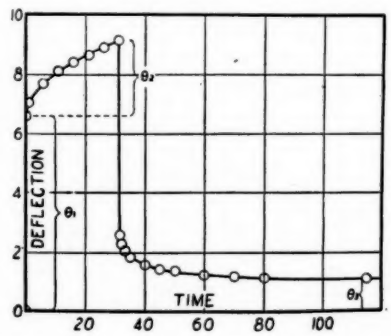

FIG. 1. The deflections (in cm on the galvanometer scale) plotted against the time (in minutes) in a typical torsion experiment with a glucose glass thread. The couple was applied here at 0 time and removed at 31 minutes.

[2] For this mode of evaluation of the modulus of rigidity see L. Page, *Introduction to Theoretical Physics* (Van Nostrand Co., New York, 1928), pp. 142, 143 and 109.

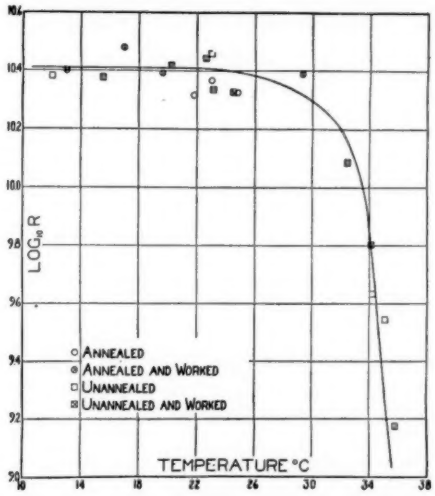

FIG. 2. The logarithm of the modulus of rigidity of some glucose glass threads plotted against the temperature.

The modulus of rigidity of the glucose glass was then calculated from these θ_1 values (converted to radians) by Eq. (1). The θ_3 values divided by the time of flow in seconds likewise yielded ω for the calculation of the corresponding viscosities by Eq. (2). The elastico-viscous effect (equivalent to $\theta_2-\theta_3$), involving as it does a decreasing elastic flow over an appreciable time interval, was thus left out of the calculations. It is an effect which has been recognized for many years in materials that possess some of the properties of both solids and liquids; but the various attempts to treat it in a theoretical way have not appeared very satisfactory.[3] If it had

[3] See for example: A. A. Michelson, J. Geol. **25**, 405 (1917); L. N. G. Filon and H. T. Jessop, Phil. Trans. Roy. Soc. **A223**, 89 (1922); V. H. Stott in W. S. Turner, *The Constitution of Glass* (Society of Glass Technology,

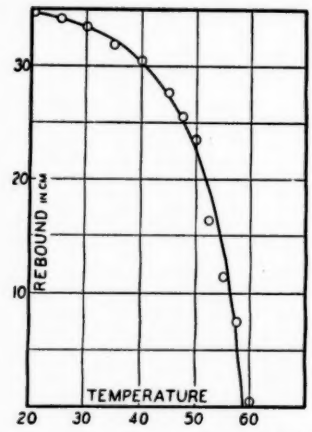

FIG. 3. The rebound distance of steel spheres, dropped from a height of 56 cm on a layer of glucose glass, plotted against the temperature.

been combined with the immediate elastic deflection in the calculations by Eq. (1), the corresponding values of R would be decreased by 35 percent on the average.

In order to maintain a constant temperature in the glucose sample during the measurements, the galvanometer was placed inside a large wooden box which was provided with a glass door in front and otherwise thermally insulated. By means of a fan, a thermoregulator and an electric heating coil within this box temperatures could then be maintained constant to $\pm 0.1°$.

After the development of the method measurements were made with about twenty-five different glucose threads within the temperature range 12°–38°C. Each specimen was used in the torsion apparatus for only one determination at a particular temperature, and then was cut into sections and weighed for proof of its uniformity. Some of these threads were used immediately after their preparation; others were first annealed at 30°–32° for several days; still others, after installation in the galvanometer, were subjected to a preliminary "working," i.e., a series of strong deflections before the actual measurements.

THE RIGIDITY RESULTS

The values of the modulus of rigidity, calculated from the immediate deflections of the galvanometer when the current was imposed, were very constant around 2.5 $(\pm 0.4)\times 10^{10}$ dynes per cm^2 over the temperature range 12°–30°C. Above 30° they fell off 94 percent within about 6° and it is clear that for this type of measurement the rigidity of glucose glass practically disappears above 36°. The experimental results are plotted in Fig. 2, from which it appears that previous annealing and working of a glucose thread produced no appreciable effect on its rigidity. Incidentally, it is of interest to note that our value of 2.5 (10^{10}) dynes per cm^2 at 20°C is only about 8 percent of the rigidity reported by Sosman[4] for vitreous silica fibers at the same temperature.

Several earlier studies[5] in this laboratory have shown that the values of some physical properties of a glass in the softening region depend greatly upon the time involved in the performance of the experiment. Thus a glass-forming substance at a given temperature may function as a solid for one type of measurement and as a very viscous liquid for another type involving a considerably greater interval of time. This point has been recently emphasized by Richards[6] in his

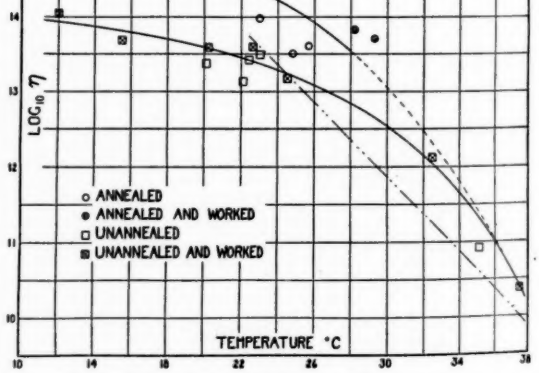

FIG. 4. The logarithm of the viscosity of some glucose glass threads plotted against the temperature. Annealed threads are represented by the upper and unannealed threads by the lower curved line. The dot-dash line represents the earlier results of Parks, Barton, Spaght and Richardson.

Sheffield, 1927), pp. 73, 155; H. Umstätter, Kolloid Zeits. **70**, 174 (1935); J. D. Ferry and G. S. Parks, Physics **6**, 356 (1935).

[4] R. B. Sosman, *The Properties of Silica* (Chemical Catalog Co., New York, 1927), p. 446.

[5] G. S. Parks, S. B. Thomas and W. A. Gilkey, J. Phys. Chem. **34**, 2028 (1930); S. B. Thomas, ibid. **35**, 2103 (1931); G. S. Parks and S. B. Thomas, J. Am. Chem. Soc. **56**, 1423 (1934).

[6] W. T. Richards, J. Chem. Phys. **4**, 449 (1936).

consideration of the thermal relaxation time of glass. In the present case, while the glucose glass above 36° has lost practically all of its rigidity in these thread torsion tests, it still retains considerable elasticity for a briefer impact test. This point was recently proved by Mr. Charles O. Yoakum, Jr. in our laboratory when he repeated the rebound experiment of Tammann and Klein[7] with a 0.2 cm layer of glucose glass resting upon a steel floor. Steel spheres (0.88 cm in diameter), when dropped from a height of 56 cm upon this layer of glucose glass, rebounded to various distances depending upon the temperature, as shown in Fig. 3. For example, the average distance of rebound was 34.7 cm at 20.5°, 27.2 cm at 45.0°, 16.4 cm at 52.5° and 0.5 cm at 60.0°C. Thus the elastic rebound did not fall to one-half of the 20° value until the temperature of the glucose reached 52°; and the rapid loss of solidity in this briefer impact test comes about twenty degrees higher on the temperature scale than with the torsion experiments on the threads.

The Viscosity Results

The viscosity values, calculated from the permanent flow by Eq. (2), ranged from 1.6×10^{15} poises at 13° for a glucose thread which had been previously annealed and "worked" to 2.4×10^{10} poises for a thread at 37.5°C. Above 32° the effect of annealing and prior working should not be very noticeable, but below 20° the annealed samples displayed on the average over ten times the viscosity of the unannealed and a preliminary working of the thread was necessary to obtain reasonably consistent results. This preliminary working led to an increase in the viscosity value in all cases, and interfered somewhat with the reliability of tests which were made to determine whether or not the glucose displayed "true" (i.e., η independent of shearing rate) viscosity at the lowest temperatures. On the whole, however, these tests seemed to indicate that the requirements of true viscosity were met, at least approximately, at 19°C.

The various viscosity results are shown graphically in Fig. 4, with two curves—the upper for the annealed and the lower for the unannealed samples. From this plot of the data it is evident that the thermal and mechanical history of a thread was all-important in determining the magnitude of its viscosity below 30° and that in this region it is impossible to assign any one value for this property at a given temperature. This point is also emphasized by the divergent position in the figure of the straight dot-and-dash line, which represents the earlier viscosity values obtained by Parks, Barton, Spaght and Richardson.[8] Between 34° and 24° these investigators used a torsion method with glucose glass cylinders of 0.83 cm diameter and 2.5 cm length, which had been annealed but not subjected to preliminary working. Even though the diameter of the cylinders was next reduced to 0.53 cm, their method failed completely below 22° on account of the excessive brittleness of the glass in this form.

Discussion

In our judgment these viscosity results throw considerable light upon the glass problem. Apparently the properties of a glass are not functions of merely two variables, such as pressure and temperature, as is the case with ordinary liquids and crystals; rather they are functions of pressure, temperature and *time* (i.e., previous history). Hence, at a given temperature and pressure there are a whole series of glucose glasses which may coexist and show considerable variations in certain properties. For this reason it is more logical to refer to the *glassy states* of glucose or of any other substance rather than to the "glassy state," as has been done by some investigators who thus have hoped to emphasize the rather marked characteristics displayed by matter in an amorphous, practically solid condition.

This concept of a series of glassy states for a substance will be discussed further in a subsequent paper.

Acknowledgment

We wish to thank Mr. Charles O. Yoakum, Jr. for the measurements on the elasticity of glucose glass by the ball-rebound method.

[7] G. Tammann and R. Klein, Zeits. f. anorg. allgem. Chemie **192**, 161 (1930); see also G. Tammann, *Der Glaszustand* (Leopold Voss, Leipsig, 1933), pp. 48–51.

[8] G. S. Parks, L. E. Barton, M. E. Spaght and J. W. Richardson, Physics **5**, 193 (1934).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

An Extension of the Analytic Method of Analysis of Electron Diffraction Photographs of Gases

In the analysis of electron diffraction photographs of gases, a generally accepted procedure[1] is to plot I *versus* x, of the function

$$I=\sum_{ij} Z_iZ_j \frac{\sin l_{ij}x}{l_{ij}x}, \tag{1}$$

for various values of the parameters l_{ij}, and to choose those values for which the corresponding curve shows the best fit with the experimentally determined intensity distribution both in general shape and in the positions of the maxima and minima. When the molecules under investigation are large and do not possess many elements of symmetry, the computations which are necessary to determine how small changes in the parameters will affect the theoretical curves become excessive since such effects cannot be calculated directly; a new curve must be obtained for every variation. An extension of the analytic method[2] is given below, which enables one to compute the trends of the changes in the curves as the parameters are given various increments.

Suppose a plot of the above function is available for a set of the parameters. The values of $x(x_m)$ at which I reaches an extremum are therefore known. Analytically, these are given by the equation

$$S=\frac{\partial I}{\partial x}=0=\sum_{ij} Z_iZ_j \frac{1}{x}\left(\cos l_{ij}x - \frac{\sin l_{ij}x}{l_{ij}x}\right)$$

so that

$$\sum_{ij} Z_iZ_j \left(\cos l_{ij}x_m - \frac{\sin l_{ij}x_m}{l_{ij}x_m}\right)=0 \tag{2}$$

is satisfied for the set x_m obtained from the curve. Suppose now that small changes in the parameters l_{ij} are made and it is desirable to find the corresponding changes in the positions of the maxima and minima. If the new parameters $p_{ij}(=l_{ij}+\Delta l_{ij})$ are substituted in (2), the equation takes the form

$$\sum_{ij} Z_iZ_j \left(\cos p_{ij}x_m - \frac{\sin p_{ij}x_m}{p_{ij}x_m}\right)=S_m \tag{3}$$

for each particular m, where S_m differs slightly from zero. A one term Taylor's expansion gives

$$(\partial S_m/\partial x_m)\Delta x_m \approx \Delta S_m \approx -S_m, \tag{4}$$

which may be solved for Δx_m when the derivative of (3) is obtained: thus,

$$\frac{\partial S_m}{\partial x_m}=-\sum_{ij} Z_iZ_j \frac{1}{x_m}\left(x_m p_{ij} \sin p_{ij}x_m+\cos p_{ij}x_m-\frac{\sin p_{ij}x_m}{p_{ij}x_m}\right).^3$$

Once the new positions of the extremal values of I are computed in terms of the new parameters, it is a simple matter to obtain the intensities at these points on the new curve through the use of the expression

$$I_m{}^1=\sum_{ij} Z_iZ_j \frac{\sin p_{ij}(x_m+\Delta x)}{p_{ij}(x_m+\Delta x)}.$$

There now arises the question of utility. Since the values of $\partial S_m/\partial x_m$ at the troughs and peaks are quite large, a small error in estimating the initial values of x_m will introduce a relatively large error in the calculation of S_m (Eq. (3)), and consequently in Δx_m. And indeed, several numerical examples demonstrate this to be the case. Although the theoretical intensity curves as they are plotted in this laboratory may be read with an accuracy which is adequate for present-day electron diffraction photographs, they are not on a sufficiently large scale to permit the use of the more sensitive procedure outlined above. Hence the purpose of this note is merely to complete the analytic method I have previously suggested. Using (3) and (4) one may calculate, in principle, the direction and magnitude of the shifts in the peaks and troughs of the scattering function and of the corresponding changes in the intensity of that function due to arbitrary variations of the parameters. The reverse problem, that is, the computing of the necessary increments in the parameters when the changes in the positions of the extremal values are given (say, as obtained from experiment), is a much more difficult one since the various x_m's are not independent so that a solution of a set of nonlinear simultaneous equations must be undertaken. A method of employing successive approximations has already been outlined.[2]

S. H. BAUER

California Institute of Technology.
Pasadena, California,
March 16, 1937.

[1] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[2] S. H. Bauer, J. Chem. Phys. **4**, 406 (1936).
[3] These calculations are simple to perform once a plot of the function $(\cos z-\sin z/z)$ and of its derivative are made. Then,

$$(\partial S_m/\partial x_m)=\sum_{ij} Z_iZ_j p_{ij}\partial/\partial z(\cos z-\sin z/z),$$

where $z=p_{ij}x_m$.

The Spectrum Characteristic of Hydrogen Bonds*

It has been observed that in certain substances containing hydroxyl hydrogen the relatively narrow and intense absorption bands which ordinarily are characteristic of the O–H group appear to be absent. Since in these cases it appears very probable that the hydroxyl hydrogen is involved in the formation of the type of linkage known as the "hydrogen bond" it has been suggested that the absence of the bands may be taken as a criterion for the presence of such bonds.[1] On the other hand the O–H fundamental band appears strongly in a number of substances containing hydroxyl groups in which the hydrogens are supposed to be engaged in linkages which Bernal and Megaw prefer, in this case, to call "hydroxyl bonds."[2] These substances include ice and a number of minerals examined by Coblentz.[3] These observations have left the situation somewhat unclear since they leave the question open as to whether the O–H absorption in the cases first mentioned has merely shifted to some new region where it has not been observed, or whether it has really disappeared. If the latter were true there would appear to be a considerable difference between the hydrogen linkages in the two cases.

In order to throw light on the question we have investigated the absorption in the photographic infrared of a number of substances which are generally accepted to contain hydrogen linkages of one sort or another. In the vapor of acetic acid, under conditions in which the material is largely dissociated into single molecules, the narrow O–H band at λ9750 was found to be intense, but as association was increased by lowering the temperature or increasing the pressure it became progressively weaker. Indeed the intensity of this band was found to be a measure of the concentration of single molecules and it was found possible to follow the association equilibrium photometrically with results in agreement with MacDougall's vapor density measurements.[4]

In dilute solutions of methyl alcohol in carbon tetrachloride and of ethyl alcohol in carbon disulfide the sharp O–H band was observed at λ9577 and λ9658, respectively, but with increasing concentration it rapidly diminished in intensity. However, in all three cases as the narrow O–H band disappeared it was replaced by new absorption regions as was observed by Errera and Mollet[5] in the region of the fundamental band in ethyl alcohol solutions. These new regions appear to be characteristic of an hydroxyl group in which the hydrogen is involved in a hydrogen bond.

We have observed similar features in the spectra of liquid ethyl acetoacetate, methyl and ethyl alcohol, sulfuric, formic and acetic acid, and of carbon tetrachloride solutions of the last two and of trichlor acetic acid. In all cases there appears a broad absorption region extending from about λ10900 to λ9700, with a maximum around λ10100. In some cases the band appears to have some structure which is best resolved in the carbon tetrachloride solutions. In the organic acids there are at least two components while in the alcohols there are four or five which simultaneously make their appearance as the solutions are increased in concentration. For this reason we believe they are not due to polymers of different sorts but to the complexity of the smallest polymers which are present in appreciable concentration.

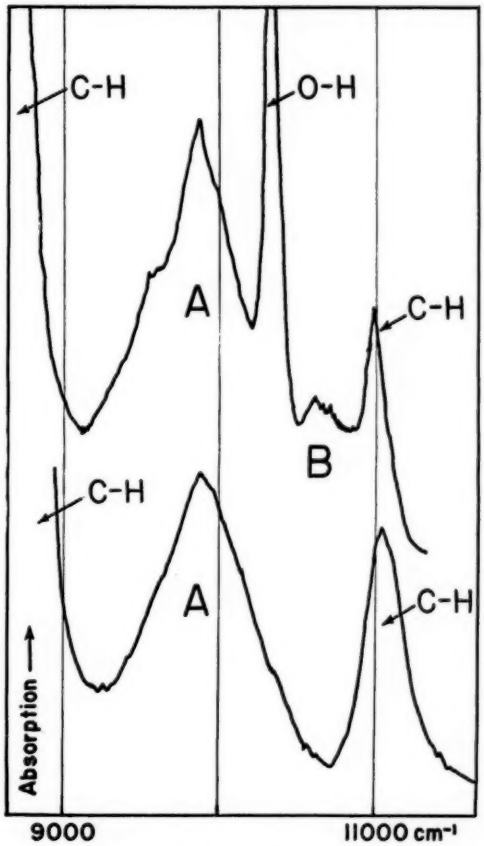

FIG. 1. Microphotometer curves showing the shift and broadening of the O–H band accompanying hydrogen bond formation. The upper curve, of a solution of ethyl alcohol in carbon disulfide at moderate concentration (10 percent by volume) shows the two bands *A* and *B* characteristic of associated alcohol molecules as well as the sharp O–H band of the single molecules. The lower curve, of ethyl acetoacetate, shows only one broad O–H band.

In the alcohols we have observed an additional absorption region on the short wave side of λ9600. This is of moderate width and relatively very weak. It is definitely absent in sulfuric acid, and in the other cases its presence is doubtful.

At first sight it appears that the O–H absorption is weakened as the hydrogen becomes involved in a hydrogen bond, but this is not at all the case and the appearance is due to the spreading out of the absorption region to at least ten times its original extent.

Since the disappearance of the narrow O–H bands as criterion for the presence of hydrogen bonds has largely been applied to aromatic compounds we have attempted observations on such substances. Unfortunately in these cases the C–H bands extend well into the region where we have found the characteristic spectrum described above and it has been difficult to draw any certain conclusions.

However, from the similarity of the results in the other cases it appears reasonable to conclude that there is a rather definite spectrum characteristic of the O–H group of which the hydrogen atom is engaged in a hydrogen bond. In the substances studied these bonds appear to be quite similar and the distinction between hydrogen and hydroxyl bonds appears to be somewhat artificial. From the rather moderate shift in the O–H frequency in the formation of the bond it appears that the binding of the hydrogen to the oxygen atom to which it originally belonged has not been greatly affected and consequently that the internuclear distance is probably only slightly larger than the normal O–H separation.

RICHARD M. BADGER
SIMON H. BAUER

Gates and Crellin Laboratories of Chemistry,
California Institute of Technology,
Pasadena, California,
March 5, 1937.

* The investigations here briefly mentioned are part of a program of research made possible by a Grant-in-Aid of the National Research Council to one of us (R. M. B.) and will be reported in detail in papers to appear shortly.

[1] Hilbert, Wulf, Hendricks and Liddel, J. Am. Chem. Soc. **58**, 548 (1936).
[2] Bernal and Megaw, Proc. Roy. Soc. London, **A151**, 384 (1935).
[3] W. W. Coblentz, *Investigations of Infra-Red Spectra* (Carnegie Institution, 1906).
[4] F. H. MacDougall, J. Am. Chem. Soc. **58**, 2585 (1936).
[5] Errera and Mollet, Nature **138**, 882 (1936).

Concerning the *Q* Branch and Analysis of the Hydrogen Sulfide Band at 10100A

Following an unsuccessful attempt to obtain more than seventeen lines in the hydrogen sulfide band at 10100A, Carvin[1] has recently questioned the validity of the previous measurement and analysis of this band.[2]

Carvin cites specifically the four strongest lines of the *Q* branch and one line of the *P* branch as definitely missing. Four of these lines were measured on all fourteen plates of the earlier work, while the fifth was measured on twelve of the fourteen plates. These lines were still observable, though greatly broadened, at pressures as high as 4 atmospheres.

An attempt is made here to reproduce portions of two of the best plates of the series upon which the original report and analysis were based. Enlargements of the original plates on process film were contact-printed on process film, and the latter printed on contrast paper. Practically all the lines reported as of intensity 2 or more are visible on these prints, as well as many of intensity 1, but considerable detail is lost in the halftone reproduction (Fig. 1). Since the original plates (Eastman type 1*Q*) were used beyond the region in which they are most suitable, they show a marked gradation in intensity which renders quite difficult their reproduction with high contrast. In addition, the slight irregularities in intensity resulting from unevenness of the supersensitization in ammonia are so enhanced as to offset a considerable portion of the gain in clarity afforded by the contrast-reproduction process.

The author wishes also to make use of this opportunity to present the evidence which convinces him that the analysis is unquestionably correct. In Fig. 2(b) are shown the observed lines which gave the clue to the analysis, and on the same scale the calculated positions of the transitions assigned to these lines. (The calculated values are from an unpublished work of Crawford and Cross in which this band is treated by the correct centrifugal distortion theory developed by Wilson.[3] The assignments are the same as in

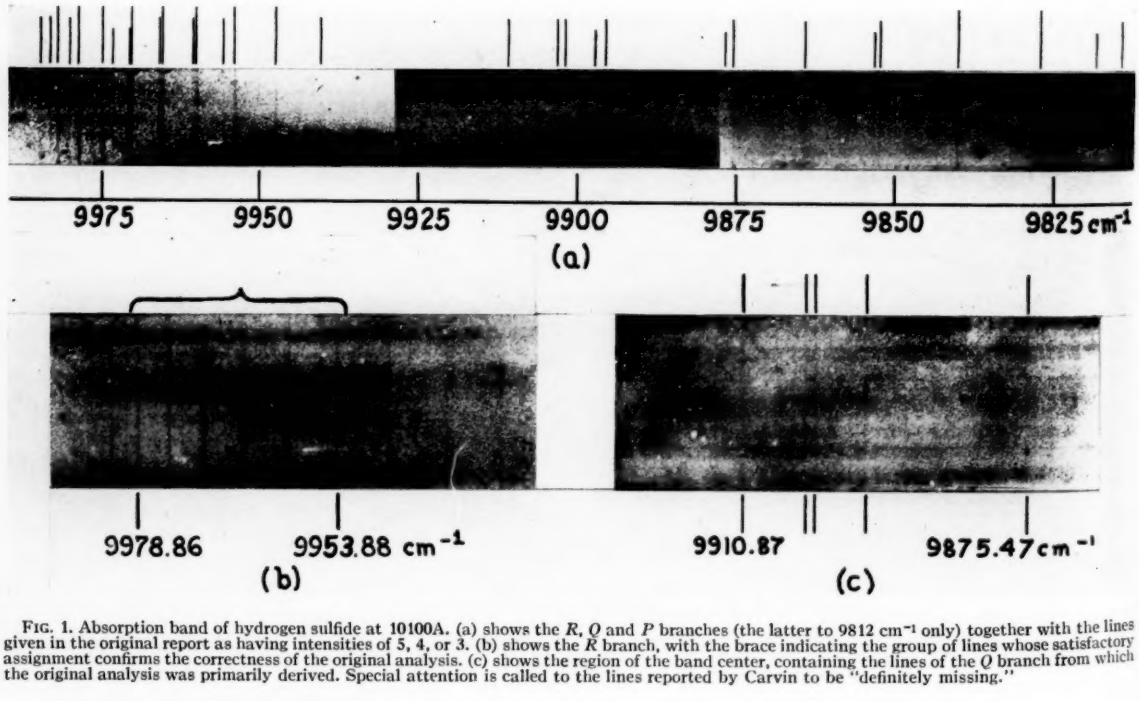

FIG. 1. Absorption band of hydrogen sulfide at 10100A. (a) shows the *R*, *Q* and *P* branches (the latter to 9812 cm⁻¹ only) together with the lines given in the original report as having intensities of 5, 4, or 3. (b) shows the *R* branch, with the brace indicating the group of lines whose satisfactory assignment confirms the correctness of the original analysis. (c) shows the region of the band center, containing the lines of the *Q* branch from which the original analysis was primarily derived. Special attention is called to the lines reported by Carvin to be "definitely missing."

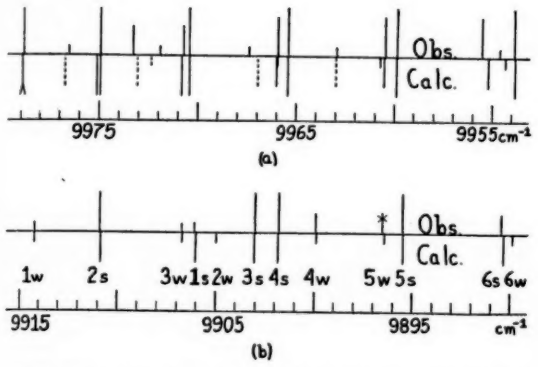

FIG. 2. Comparison of observed and calculated transitions. (a) Region marked by the brace in Fig. 1 (b). The heights of the observed lines are proportional to their intensities (reference 2). Calculated lines originating in levels antisymmetric with respect to the hydrogens are given length 3, while those from symmetric levels are given length 1. Unresolved pairs are given length 4. The full lines indicate transitions of the type $j_{-j+i} \rightarrow (j+1)_{-j-1+i}$, with $i=0$, 1, 2, or 3. Dotted lines represent transitions for which $i>3$, and are included for the sake of completeness. Detailed assignments may be found in reference 2. (b) Q branch lines of the type $j_j \leftrightharpoons j_{j-1}$. Intensities indicated as in Fig. 2 (a). s and w refer to the strong and weak components, respectively, of the pair of lines for a given value of j. The line marked with an asterisk was not given in the original report of this band, but has been located on the reproductions required for this communication.

the former analysis using the classically corrected Wang equation, and only slight changes in the calculated positions are introduced.) Certainly the agreement is all that could be desired. When this region was satisfactorily explained, the unusual "doublet" structure of certain lines in the R branch was automatically accounted for. The observed and calculated lines of this region (marked by the brace in Fig. 1(b)) are shown in Fig. 2(a).

PAUL C. CROSS

Stanford University,
Stanford University, California,
March 31, 1937.

[1] F. D. Carvin, J. Chem. Phys. **5**, 159 (1937).
[2] P. C. Cross, Phys. Rev. **47**, 7 (1935).
[3] E. B. Wilson, Jr., J. Chem. Phys. **4**, 260 (1936), and by private communication of unpublished details of the centrifugal expansion treatment.

The Valence Angle in Hydrogen Sulfide

In a recent publication, Sprague and Nielsen[1] have presented data on the infrared spectrum of H_2S which is interpreted as favoring a valence angle of about 85° rather than 92° as previously reported from the rotational analysis of the band at 10100A.[2] The 92° angle may be established by applying the following intensity considerations to the Q branch of this band.

In complete analogy to the case of the H_2 molecule, the rotational wave functions for the H_2S molecule may be divided into two classes: those symmetric and those antisymmetric with respect to interchange of the hydrogen nuclei.[3] In the ground state of H_2S, the antisymmetric states have a statistical weight factor three times that of the symmetric states, and hence lines originating in antisymmetric ground states are approximately three times as strong as analogous lines originating in symmetric states. With an angle of 92°, interchange of the hydrogen nuclei is effected by a rotation through 180° about the axis of intermediate moment of inertia, and the symmetry character of a given rotational state is given by the product of Dennison's symmetries (a) and (b).[4] Applied to the Q branch at 10100A, this reasoning yields the intensity pattern plotted in Fig. 2 of the preceding letter, in agreement with the observed intensities.

If the angle were 85°, interchange of the hydrogen nuclei would be effected by a rotation through 180° about the axis of least moment of inertia, and the symmetry character would be given by the second of Dennison's symmetries, (b). This would require that both transitions of the type $j_i \rightleftarrows j_{j-1}$ be strong for odd values of j and weak for even values of j, in complete disagreement with the observed intensities.

The argument for the 85° angle is partially based on what the authors consider to be an erroneous interpretation of the band at 3.7μ.[5] The suggestion of Sprague and Nielsen that the band center lies near 2685 cm^{-1} yields an average spacing incompatible with the previously derived moments of inertia.[2] Furthermore, the sharpness and high intensity of the lines near 2685 cm^{-1} cannot be reconciled with the typical appearance of rotational bands, either with or without a collected Q branch. On the other hand, the spacing, convergence, and intensities of the observed lines are in satisfactory agreement with the R branch of either ν_σ (ν_3) or ν_π (ν_1) calculated from the known constants for the normal state and constants approximately 1.3 percent smaller for the excited state. (The factor of 1.3 percent was suggested by a rough interpolation between the normal state and the excited state of the 10100A band.) This calculation would place the band center between 2600 and 2620 cm^{-1}; the apparent weakness of the absorption in this region would indicate the absence of a collected Q branch, and hence would require that this band be assigned to ν_π. However, the present unsettled status of the P branch[1, 5-7] makes it very unsafe to draw any definite conclusions based on the apparent absence of a collected Q branch.

Sprague and Nielsen also base their argument on the apparent collected Q branch in the 8.0μ band, which must certainly be assigned to δ_π (ν_2). The oscillation of the electric moment in this vibration is along the symmetry axis, which would accordingly be the axis of least moment of inertia. The authors believe that an alternative explanation of the appearance of this band may be found in the pronounced changes in the least and intermediate moments of inertia which would be expected in this mode of vibration. These changes would produce a pattern markedly different from that of the simplified charts given by Dennison.[3]

These factors, together with certain discrepancies in the data so far reported, make a complete vibrational analysis difficult at this time.

BRYCE L. CRAWFORD, JR.
PAUL C. CROSS

Stanford University,
Stanford University, California,
April 12, 1937.

[1] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937).
[2] P. C. Cross, Phys. Rev. **47**, 7 (1935).
[3] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[4] D. M. Dennison, Rev. Mod. Phys. **3**, 324 (1931).
[5] H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931).
[6] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **43**, 375 (1933).
[7] C. R. Bailey, J. W. Thompson and J. B. Hale, J. Chem. Phys. **4**, 625 (1936).

The Use of Deutero Compounds as Indicators for the Presence of Free Radicals in Organic Decomposition Reactions

There is at present considerable uncertainty regarding the importance of free radicals in organic decomposition reactions. Information on this point is particularly desirable in the case of substances which decompose by a first-order mechanism. It is certain that radicals do participate in decomposition processes at high temperatures, and that they can often exert a sensitizing effect on other reactions. It also seems certain, however, that the predictions of the free radical chain theory regarding stationary concentrations of atoms and radicals, and the activation energies of elementary processes are frequently definitely in disagreement with the facts. It is therefore desirable to have as many independent methods of investigating the question as possible.

We have recently carried out experiments in which a mixture of two organic compounds is decomposed. In one of the compounds all the hydrogen atoms have been replaced by deuterium. If decomposition occurs by a molecular mechanism, the products of the decomposition of one compound should be entirely "light," and those of the other entirely "heavy." If, however, free radicals or atoms intervene, then cross products will be formed. It should therefore be possible to obtain considerable information concerning the mechanism of the decomposition from an examination of the deuterium distribution among the products.

Thus mixtures of deutero-acetone and ordinary dimethyl ether have been decomposed at 590°C. The general course of the decompositions is known to be

$$CD_3COCD_3 = CD_4 + CD_2 = CO = CD_4 + CO + \tfrac{1}{2}C_2D_4$$
$$CH_3OCH_3 = CH_4 + HCHO = CH_4 + CO + H_2.$$

It follows, therefore, that the hydrogen from the products should be all light if the process goes as indicated. If, however, formaldehyde decomposes by $HCHO = H + CHO$, then the resulting hydrogen atom is as likely to extract another atom from the ether as from acetone, so that there should be approximately equal chances of getting HD and H_2. Hence, on a radical mechanism, we would expect the hydrogen to be approximately 25 percent heavy.

The actual investigation is complicated by the fact that hydrogen from the decomposition of methyl ether will slowly exchange with the products of the acetone decomposition. This effect, however, is not great if short contact times are used, and can be corrected for by blank experiments. The result found is that within an experimental error of about 2 percent the hydrogen from the mixture decomposition is entirely light.

Thus in a number of experiments a mixture of acetone (48.3 percent heavy) and methyl ether was heated at 590°C for 5 minutes and then withdrawn and the hydrogen separated and analyzed. The mean deuterium content found was 3.3 percent. In blank experiments acetone and ether were decomposed separately, and the products were mixed and heated to 590°C for 5 minutes. The mean deuterium content of the hydrogen in this case was 2.1 percent.

It may therefore be concluded that formaldehyde does not decompose by a free radical mechanism, since it is very unlikely that the reaction $H + CD_3COCD_3 = HD + CD_2COCD_3$ should have a very much slower rate than that of $H + CH_3OCH_3 = H_2 + CH_3OCH_2$. Indeed Rice estimates the former to be the faster, and in any case it appears probable that reactions of this type have very low activation energies, and hence collision yields not far from unity at 590°. This is in agreement with the results of Patat and Sachsse[1] who found a negligibly small stationary H atom concentration during the decomposition of formaldehyde.

Fletcher and Rollefson[2] have pointed out that formaldehyde formed as an intermediate in the decomposition of methyl ether itself decomposes about 15 times faster than normal. They suggest that this is due to a sensitized decomposition by methyl radicals from the ether decomposition, *viz.*

$$CH_3 + HCHO = CH_4 + CHO,$$
$$CHO = CO + H.$$

Since this would also involve the occurrence of free H atoms, our experiments cast considerable doubt on this explanation.

Our results also seem to preclude the possibility of a very high concentration of methyl radicals during the methyl ether decomposition, since otherwise the reaction $CH_3 + H_2 = CH_4 + H$ would be expected to come into play.

It is, of course, too early to draw sweeping conclusions from the results, but the method seems to have possibilities. The work is being continued with more accurate analytical methods.

This work has been done with financial assistance from the National Research Council of Canada, and one of us (W. A. A.) wishes to acknowledge the receipt of a Bursary from the same source.

E. W. R. Steacie
W. A. Alexander

Physical Chemistry Laboratory,
McGill University,
Montreal, Canada.

[1] Nach. Ges. Wiss. Göttingen **1**, 41 (1935).
[2] J. Am. Chem. Soc. **58**, 2129 (1936).

Effect of CS_2 as Solvent On Electric Moment of Solute

In a recent article[1] the writer reported data from measurements of the polarization of ethyl alcohol in extremely dilute solutions using benzol and carbon tetrachloride as solvents. It was reported that measurements had been made on solutions of ethyl alcohol dissolved in carbon disulfide but the polarization of the alcohol as obtained from these solutions was not reported because of slight deviations of the P_2C_2 *versus* C_2 curve from linearity which were attributed to some possible chemical reaction between the carbon disulfide and the brass condenser. The electric moment of alcohol was not calculated from these data.

Recently the writer received a private communication from K. Higasi who stated that he had measured the polarization of isopropyl and isobutyl alcohol in carbon disulfide and had obtained values of electric moment equal to 1.41 and 1.48 (times 10^{-18} e.s.u.), respectively, which did not compare favorably with values of μ equal to 1.70 times 10^{-18} e.s.u. for both substances obtained by him[2] from data on benzol solutions.

Using the previously mentioned unreported data on twenty-eight solutions of ethyl alcohol in carbon disulfide ranging in concentration from 0.0045 to 0.9 mole percent the writer has obtained values of electric moment of ethyl alcohol of μ equals 1.51 times 10^{-18} e.s.u. from solutions in which specially purified carbon disulfide was used, and μ equals 1.55 times 10^{-18} e.s.u. from solutions in which the carbon disulfide was not specially purified by the writer. These values must be compared with μ equals 1.70 times 10^{-18} e.s.u. from benzol solution and μ equals 1.67 times 10^{-18} e.s.u. from carbon tetrachloride solution.

Thus the values μ as obtained from carbon disulfide solutions were low by approximately the same amount in both of the above cases, but the discrepancies obviously cannot be attributed to chemical reaction between the material of the condenser and the solvent since Higasi reports the use of a platinum condenser. It seems impossible to attribute the low value to the presence of an impurity such as water vapor since it is believed to have been completely removed by the writer from the specially purified reagent which gave the lower value of μ.

The writer now has under construction a completely new set of apparatus with which it is hoped to attain even greater precision of measurements for the investigation of this effect.

FRANK E. HOECKER

Department of Physics,
University of Kansas City,
Kansas City, Missouri,
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[1] J. Chem. Phys. **4**, 431 (1936).
[2] Sc. Pap. I. P. C. R. **28**, 284 (1936).